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THE CHEMICAL SOCIETY.

PAPERS READ BEFORE THE CHEMICAL SOCIETY.

I.—*A Chemical Study of Vegetable Albinism.* Part II. *Respiration and Transpiration of Albino Foliage.*

By A. H. CHURCH, Professor of Chemistry at the Royal Academy of Arts in London.

NOTWITHSTANDING the lack of sunshine during the summer months, I have been enabled to make a few determinations of the influence of certain white leaves upon the composition of the surrounding air. In my previous paper, published in the Journal of the Society for January last, I expressed a hope that I should be able to determine during the summer of 1879 "the exact relations of equal areas of white and green foliage to carbon dioxide, oxygen, and moisture." A part, and a very small part only, of the contemplated work has been accomplished, yet enough has been done to verify the general view, expressed in my previous memoir, as to the relations of albino to ordinary foliage. Thanks to a further donation from the Government Research Fund, and to the renewed permission from Sir J. D. Hooker to use the Jodrell Physiological Laboratory in the Royal Gardens at Kew, I have proved that white foliage does not possess the power, in strong daylight or even in actual sunshine, of decomposing the carbon dioxide of the air. On the contrary, I found that albino leaves add largely to the normal amount of that gas in the air, thus behaving like the petals of flowers, or like green leaves during darkness. Owing to many untoward circumstances, the experiments were not begun as early in the summer as was desirable; nor was the arrangement of the apparatus exactly suited to the purpose in view. But at all events

the experiments on white leaves are comparable with those on green, though both lack that exact quantitative character which I had wished to impress upon them. A few words upon the plants and apparatus employed, and upon the conduct of the experiments, may be given by way of introduction.

The plants selected for trial included four of those subjected to analysis in my previous investigations on vegetable albinism. I began with *Cyperus alternifolius*, and, not obtaining very decisive results with that plant, worked with *Acer Negundo*, *Ilex Aquifolium*, *Hedera Helix*, and *Alocasia macrorrhiza*. The last-named plant was in most active growth, and yielded by far the best results. In some of the other experiments even the green parts of the plants employed added slightly to the CO₂ originally present in the air of the containing vessel, by reason of the advanced period of the summer and the maturity of the foliage. In fact some of the later processes of vegetable metastasis were doubtless occurring, while the assimilation of CO₂ and fixation of carbon were languid, if they had not ceased altogether.

Every endeavour was made to secure such specimens of albino and of normal foliage as admitted of fair comparison in all particulars. When a green patch in an otherwise white leaf, or a white patch in an otherwise green leaf, required "stopping out," a coating of collodion was employed with success, no interference with the accuracy of the experimental results being thereby introduced.

The leaf-stalks were placed in tubes of different and suitable heights containing recently boiled distilled water which had been cooled out of contact with the air. These tubes were arranged in a weighted beaker standing in a dish of mercury. The leaves so arranged were covered with a large bell-jar, and allowed to stand at rest for a quarter of an hour before beginning each experiment. The bell-jar employed was fitted with a cork and two tubes, one nearly touching the mercury in the dish below, the other terminating just inside the cork. A Pettenkofer's absorption tube, about three feet long, is filled with baryta-water, perfectly bright and clear, in the following manner. The tube is carefully rinsed with distilled water, and then air is drawn slowly though it, the air passing first through a U-tube containing potash attached to the bulb-end of the absorption tube. A 1½ per cent. solution of barium hydrate is kept in a bottle provided with a syphon, which is now to be connected with the smaller end of the absorption tube. The syphon delivers the baryta solution until the tube is about three-quarters full, when it is detached and the absorption tube instantly closed with a glass stopper. It is now connected with the longer tube of the bell-jar, and is thus placed in communication with the air surrounding the leaves. At the other end of the apparatus an aspirator is attached to the potash tube, and air is drawn

through at the rate of about $2\frac{1}{2}$ litres per hour. When an experiment is terminated, it is necessary to adopt a special plan for the removal and washing, out of contact with the air, of the BaCO_3 formed: the following plan was employed. A beaker with funnel and filter is supported over a dish of potash solution. This arrangement floats on a surface of mercury contained in a larger dish. It is covered by a large bell-jar, which is closed below by mercury. The neck of the bell-jar is furnished with an india-rubber stopper, in which are inserted two tubes, one of them reaching nearly to the surface of the potash solution named above, the other (which is drawn out below to a jet) is situated just over the filter. After giving the CO_2 in the apparatus time to be absorbed by the potash solution (to avoid delay air may be drawn through by means of an aspirator), the absorption tube is connected with the jet tube in the jar by means of a piece of india-rubber tubing sufficiently long to allow of free movement in the subsequent washing operations. The precipitated BaCO_3 is thus conveyed to the filter, where it is washed with a hot saturated solution of barium carbonate, and at last with a little distilled water, the potash guard-tube from the bulbed extremity of the absorption tube being for a moment dismantled in order to introduce the washing liquids. The bell-jar may now be removed, and the precipitate on the filter dissolved in dilute hydrochloric acid, the absorption-tube being also rinsed with a little HCl , as it may contain a few particles of adherent BaCO_3 . The acid solutions are united, the washings of tube and filter added, and the whole evaporated to a small bulk and transferred to a platinum vessel. A few drops of pure sulphuric acid are now introduced, and the whole mixture is then evaporated to dryness and ignited. I introduce these details once for all in order to avoid further reference to the description of the process as given by Drs. Dupré and Hake in the *Society's Journal* for March, 1879.

Two preliminary experiments were necessary previous to commencing my investigation as to the relations of albino foliage to CO_2 . It was necessary to determine the proportion of CO_2 normally and usually present in the air of Kew Gardens; it was necessary to learn, by a blank experiment, what was the probable experimental error of each baryta determination as made by the above described process.

The first of these two determinations was conducted on the lawn outside the Jodrell Laboratory, at three feet from the ground. On the 27th August, rain falling at the time, and the temperature being 17.5°C ., the following figures were obtained:—

2570 c.c. of air, or 2420 c.c. at 0°C ., gave .0077 gram BaSO_4 , equal to .00145 gram CO_2 , or 3.05 volumes of CO_2 per 10,000 of air at 0° .

A second experiment on a dull day with the thermometer at 21.5° —

5140 c.c. of air, or 4770 c.c. at 0° C., gave .016 gram BaSO₄, equal to .00302 gram CO₂, or 3.21 volumes of CO₂ per 10,000 of air at 0°.

It will probably be regarded as sufficiently accurate for the purposes of the present inquiry if we accept 3.13 parts of CO₂ per 10,000 as normally present in the air during the time of our experiments of the past autumn. But when a blank experiment was made with 5140 c.c. of air at 19° C. during a fine day, it was found that the air, previously deprived of CO₂ by passing through two U-tubes of potash, gave a final product of .003 gram BaSO₄ at the conclusion of the whole series of operations. This corresponds to .59 volume of CO₂ per 10,000 volumes of air at 0°, and must be regarded as due to experimental errors connected with the process. I have not, however, thought it worth while to deduct this quantity of CO₂ from my analytical results, as they cannot pretend to that degree of accuracy which identity of all the conditions could alone secure. The sunshine available was occasional and capricious; the time occupied in each experiment was unavoidably varied, while the whole atmosphere in which the various leaves submitted to experiment had been immersed, was in no case operated on so as to determine the composition of that portion of it which remained in the jar at the close of each experiment. All one can say from the experimental data gathered into the following table, is that growing albino foliage even in sunshine adds largely to the CO₂ in the air, green foliage under nearly or quite the same conditions of temperature, time of year, exposure, moisture, flow of air, adds but little CO₂ or reduces its proportion.

Name of Plant.	Duration of Expt.		Duration of Sunshine.		Temperature.	Vol. of air passed over calculated at 0°.	Weight of BaSO ₄ obtained.
		H. M.	H. M.		C.	c.c.	gram.
<i>Cyperus alternifolius</i>	white ..	2 30	0 10		17	4840	.0152
	white ..	1 10	None		17	2420	.0103
	green ..	2 0	None		19	4800	.0052
<i>Acer Negundo</i>	white ..	2 6	1 48		20	4790	.1050
	green ..	2 5	1 45		21	2385	.0092
<i>Ilex Aquifolium</i>	white ..	2 7	2 5		21	4770	.1088
	white ..	1 5	None		17.5	2415	.0235
	green ..	1 50	1 50		24.7	4700	.0412
<i>Hedera Helix</i>	white ..	2 0	0 30		19	4800	.0400
	green ..	1 45	0 35		17.5	4830	.0120
<i>Alocasia macrorrhiza</i>	white ..	2 10	1 0		18.4	4815	.0435
	white ..	1 15	0 18		17.5	2415	.0875
	green ..	1 50	1 50		18.7	4800	.0190

Name of Plant.	CO ₂ by weight in 10,000 c.c. of air.	CO ₂ by measure in 10,000 parts of air.	Surface of leaves in square centims.	During the expt. 1,000 sq. centims. produced or abstracted parts of CO ₂ in 10,000 air.	
	gram.	c.c.			
<i>Cyperus alternifolius</i> { white ..	·00593	3·01	476	-0·25	white
{ white ..	·00801	4·06	476	1·89	white
{ green ..	·00204	1·04	333	-6·28	green
<i>Acer Negundo</i> { white ..	·04050	20·56	1045	16·69	white
{ green ..	·00725	3·68	1229	0·44	green
<i>Ilex Aquifolium</i> { white ..	·04306	21·85	942	18·82	white
{ white ..	·01835	9·32	818	7·56	white
{ green ..	·01655	8·40	1174	4·49	green
<i>Hedera Helix</i> { white ..	·01580	8·02	788	6·21	white
{ green ..	·00470	2·38	880	-0·85	green
<i>Alocasia macrorrhiza</i> { white ..	·01705	8·65	300	15·06	white
{ white ..	·02920	14·82	300	38·96	white
{ green ..	·00745	3·78	567	1·14	green

The loss of water suffered by albino foliage as compared with green foliage, was studied by means of four experiments on white and green holly leaves. It was found that a number of sprays, 38·39 grams in weight, of pure white holly, when placed in separate vessels of water in diffused daylight out of doors, gained ·11 gram in two hours, while 50·31 grams of similar sprays of green holly, exposed under the same conditions, and at the same time, gained ·77 gram. The gain of the white leaves was thus only ·29 per cent. (and doubtless they lost some CO₂), but the green acquired an increase of 1·55 per cent., part of the latter being explicable if some fixation of carbon as well as absorption and retention of water had occurred. But when no water was supplied to a second series of white and green holly sprigs, there was a loss of 6·54 per cent. in 3½ hours' exposure (during five minutes of which the sun shone) in the case of the white leaves, while the green leaves lost under the same conditions no less than 10·26 per cent. of their original weight, the much more aqueous white leaves transpiring water less readily than the drier green foliage of the same plant. The weights of white and green leaves employed in this second set of experiments were :—

	Before exposure.	After 3½ hours' exposure.
White	36·22 gram.	33·85 gram.
Green	63·75 ,,	57·21 ,,

The slowness with which albino foliage loses its moisture is quite in accordance with the observations and analyses recorded in my previous paper on Vegetable Albinism.

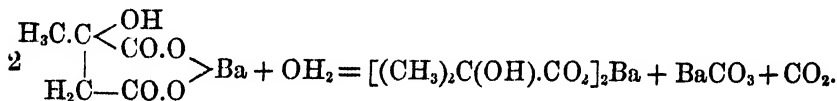
Further study of the chemistry of growing albino foliage must be deferred until another and, let us hope, more propitious summer, supplies one of the most necessary conditions of success. Many data remain to be determined, and I must apologise for the very imperfect account of the respiration and transpiration of albino foliage which I have submitted to your notice in the present communication. The subject is a large one and quite new; in many directions I perceive that it demands further investigation.

I must thank Mr. C. Rawson, jun., for his continued assistance this autumn in the conduct of the experiments, while I am again deeply indebted to Sir J. D. Hooker and the officials of the Royal Gardens, for the kind aid which has been afforded me in this research.

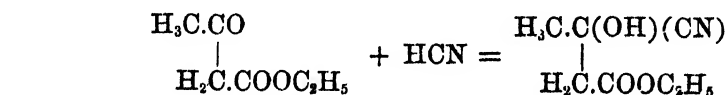
II.—On α -Methyl-hydroxysuccinic Acid, the product of the Action of Anhydrous Hydrocyanic Acid upon Ethyl Aceto-acetate.

By GEORGE H. MORRIS.

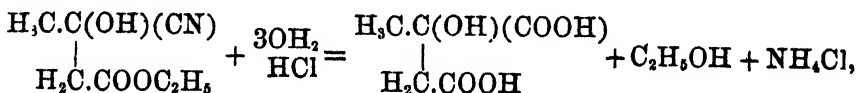
DEMARÇAY (*Compt. rend.*, 82, 1337) has described, under the name of oxypyrotartaric acid, the acid obtained from ethyl aceto-acetate by the action of anhydrous hydrocyanic acid, and decomposition of the resulting cyanide by boiling with acids. He states that the acid so obtained is an unstable, uncrystallisable syrup, and that the barium salt, when boiled with excess of water, is decomposed, carbonic anhydride being evolved, and barium carbonate precipitated, whilst the barium salt of a different acid, viz., hydroxyisobutyric acid, remains in solution. He gives the following equation for this decomposition:—



From the mode of formation of this acid, as shown by the following equations—



and



it is the next higher homologue of malic acid, the salts of which are well-defined and crystalline, thus:—



It would therefore appear probable that such an acid would be a stable compound, yielding well-defined salts. On this account, at the suggestion of Prof. Wislicenus, I undertook to go over the work of Demarçay, in order to obtain more conclusive evidence of the nature of this acid.

Preparation of the Acid.

I prepared the acid, according to Demarçay's directions, by heating a mixture of 2 parts of pure ethyl aceto-acetate, and 1 part of anhydrous hydrocyanic acid in sealed tubes for three days, at 100°. The tubes were then opened, and the light brown contents heated on a water-bath for some time, to expel the excess of hydrocyanic acid. The cyanide so obtained was then mixed with about twice its weight of rather dilute hydrochloric acid, and boiled for some time in a flask connected with an inverted condenser. When the decomposition was complete, the liquid was evaporated to drive off the excess of hydrochloric acid, and also the alcohol formed in the reaction. The mixture of ammonium chloride and acid remaining after evaporation was shaken with dry ether, in order to extract the acid, and the ethereal solution filtered from ammonium chloride; this was repeated until the whole of the acid was extracted; and the ethereal solution was then evaporated on a water-bath, when the acid was left as a thick brown syrup. To purify this impure product, it was dissolved in water, neutralised with ammonium hydrate, and basic lead acetate added to precipitate the lead salt. This was collected on a filter, thoroughly washed, then suspended in water, and decomposed by passing a stream of sulphuretted hydrogen through the liquid. The solution of purified acid was filtered from the lead sulphide formed, and concentrated to a small bulk on a water-bath. This concentrated solution was then shaken with ether several times. The syrupy acid, obtained by evaporating these ethereal solutions, was still slightly coloured; it was allowed to stand for a few days in a vacuum over sulphuric acid, when it set to a crystalline mass. The completely dried mass was again dissolved in dry ether, filtered from a little insoluble matter, and evaporated as before. The pure crystalline acid so obtained was dried in a vacuum until it ceased to lose weight, and was then analysed. It gave the following numbers:—

I. 1.448 gram acid gave on combustion 2.160 gram CO_2 , and 0.745 gram OH_2 .

II. 1.990 gram gave 2.975 gram CO_2 , and 1.000 gram OH_2 .

Calculated for $\text{C}_5\text{H}_8\text{O}_6$.				Found.	
				I.	II.
C_5	60	40.54		40.67	40.77
H_8	8.	5.40		5.72	5.58
O_6	80	54.05		—	—
	<hr/>	<hr/>			
	148	99.99			

The acid is very deliquescent, easily soluble in water, alcohol, and ether, and crystallises, on standing over sulphuric acid or in a vacuum, from its solution in these solvents, in star-like groups of needles. It melts at 108° , and is decomposed at a higher temperature.

Salts of the Acid $\text{C}_5\text{H}_8\text{O}_6$.

The free acid gives no precipitate with neutral or acid lead acetate solution, but is completely precipitated by basic acetate. A solution of a neutral salt gives a white precipitate with basic acetate of lead, and also with nitrate of silver solution, but with neutral lead acetate or with barium hydrate it gives no precipitate.

Barium Salt.—This salt was prepared by neutralising a strong solution of the acid with barium carbonate, evaporating the solution to a small bulk on a water-bath, and finally allowing the concentrated solution to stand over sulphuric acid until it was quite dry. So obtained, it is a transparent, non-crystalline, glassy, deliquescent mass, and contains 2 molecules of water, which it loses at 150° . The analysis of the perfectly dried salt gave the following results:—

2.128 gram salt lost on drying at 150°C . 0.239 gram, = 11.23 per cent.

Calculated for $\text{C}_5\text{H}_8\text{BaO}_6, 2\text{OH}_2$.		Found.
OH_2	11.28 per cent.	11.23

I. 2.901 gram of the 150° dried salt gave on combustion 1.798 gram CO_2 , 0.547 gram OH_2 , and 1.987 gram BaCO_3 .

II. 3.244 gram gave 2.153 gram CO_2 , 0.640 gram OH_2 , and 2.219 gram BaCO_3 .

III. 2.156 gram salt gave 1.466 gram BaCO_3 .

IV. 5093 ,, 3488 ,,

Calculated for $C_5H_6BaO_5$.		Found.			
		I.	II.	III.	IV.
C	60 21·20	21·07	21·42	—	—
H	6 2·12	2·09	2·09	—	—
Ba	137 48·41	47·63	47·57	47·73	47·64
O	80 28·27	—	—	—	—
	<hr/> 283 100·00				

In order to test Demarçay's statement that the barium salt was decomposed on boiling with water, a solution of the free acid was neutralised with barium hydrate and boiled for several hours. No decomposition, however, took place, the solution remained perfectly clear, and no gas was evolved. The solution, after boiling, was evaporated to dryness, the salt dried at 150° until it ceased to lose weight, and analysed. It gave the following numbers:—

I. ·4670 gram salt gave on combustion ·2937 gram CO_2 , ·0940 gram OH_2 , and ·3268 gram $BaCO_3$.

II. ·3450 gram gave ·2107 gram CO_2 , ·0722 gram OH_2 , and ·2381 gram $BaCO_3$.

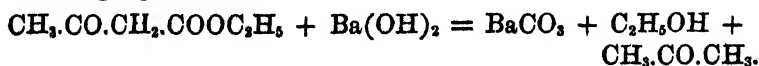
III. ·5480 gram salt gave ·4545 gram $BaSO_4$.

Calculated for $C_5H_6BaO_5$.		Found.		
		I.	II.	III.
C	21·20	21·44	20·86	—
H	2·12	2·23	2·32	—
Ba	48·41	48·63	48·00	48·72
O	28·27	—	—	—

The formula for the barium salt of hydroxyisobutyric acid gives the following percentage:—

C_8	96	27·99
H_{14}	14	4·08
Ba	137	39·95
O_6	96	27·99
	<hr/> 343	<hr/> 100·01

The acid obtained by Demarçay probably contained a little undecomposed ethyl aceto-acetate, which I found would prevent the acid from crystallising, and would also, if the barium hydrate was in excess, cause the precipitation of barium carbonate on boiling the solution of barium salt. The acetate, boiled with barium hydrate, would saponify, as shown by Wislicenus (*Liebig's Annalen*, 186, 166), according to the following equation:—



Calcium Salt.—This is best prepared by neutralising a solution of pure acid with calcium carbonate. It is extremely soluble in water, and is obtained as a deliquescent, crystalline mass by long standing of its concentrated solution over sulphuric acid.

Potassium Salt.—This salt is also extremely deliquescent. It was only obtained crystalline by allowing a strong solution to stand for several months over sulphuric acid. It was prepared by neutralising a solution of the free acid with pure potassium hydrate.

Silver Salt.—When silver nitrate solution is added to a solution of the potassium salt, a white bulky precipitate is formed, which is soluble in hot water. On allowing the hot solution to cool, the salt crystallises out in plates, which blacken on exposure to light. These crystals when thoroughly dried, gave the following numbers on analysis:—

I. 1930 gram salt gave on combustion 1145 gram CO_2 , 0330 gram OH_2 , and 1130 gram Ag.

II. 1440 gram salt gave 0850 gram CO_2 , 0250 gram OH_2 , and 0845 gram Ag.

Calculated for $\text{C}_5\text{H}_6\text{Ag}_2\text{O}_5 + \frac{1}{2}\text{OH}_2$.			Found.	
			I.	II.
C_5	60	16.17	16.10	16.12
H_7	7	1.88	1.92	1.90
Ag_2	216	58.22	58.68	58.55
$\text{O}_{\frac{1}{2}}$	88	23.72	—	—
	<hr/>	<hr/>		
	371	99.99		

As the salt is decomposed when heated below 100° , the water of crystallisation could not be directly determined.

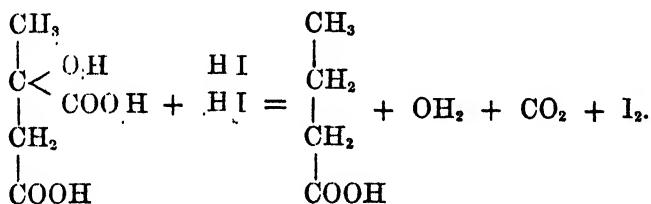
Lead Salt.—A solution of the free acid or of the neutral salt gives no precipitate with neutral acetate of lead; but when lead acetate is mixed with a neutral salt, and then a few drops of ammonia added, or better, by the direct addition of basic acetate solution, a dense white precipitate is thrown down, which is not dissolved when the liquid is boiled, but becomes granular. The salt so obtained consists of a basic salt, and appears to have the formula $\text{C}_5\text{H}_6\text{PbO}_5\text{PbO}$. I found it impossible, after repeated experiments, to get a pure neutral salt fit for analysis. The experiments always resulted in a more or less basic salt.

Copper Salt.—This was prepared by boiling a solution of the acid with excess of copper carbonate and filtering the solution. This salt is also very deliquescent, and on leaving its solution over sulphuric acid, it is obtained as a transparent, blue, glassy mass. It was also found impossible to obtain this salt neutral, it being always, to a greater or less extent, basic.

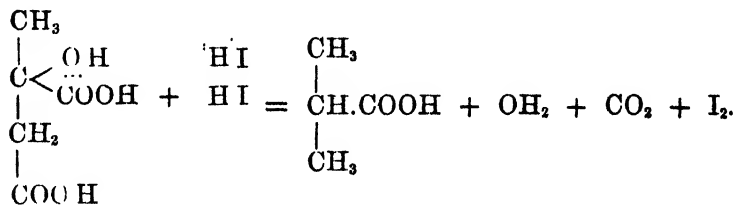
Reduction of Acid with fuming Hydriodic Acid.

About 6 grams of the acid were heated with six times its weight of fuming hydriodic acid in a sealed tube to 130° — 140° for six hours. When cold, the tube was opened—there was a moderate pressure in the tube and smell of butyric acid—and the contents shaken with mercury to remove the free iodine, which was present in large quantity. The nearly colourless liquid was then evaporated to a small bulk, it being thought that the product of the reduction would be pyrotartaric acid, which is not volatile; the small quantity of watery solution was shaken with pure ether, and the ethereal solution separated and evaporated on a water-bath. After evaporation, only the merest traces of organic matter remained. The watery liquid, from which the ether had been separated, was then examined, but nothing organic was found in it; so that the conclusion arrived at was that the product had been dissipated in evaporation. The reaction is probably expressed by the following equation; the pyrotartaric acid first formed, splitting up, under the influence of hydriodic acid, into either butyric or isobutyric acid and carbonic anhydride:—

Either



or



As the evaporations were performed in a draft cupboard, there was no opportunity of noticing the butyric acid as it was driven off.

Dry Distillation of the Acid.

A portion of the acid was placed in a small distillation-flask connected with a suitable condenser, and distilled from an oil-bath. The acid was decomposed at about 140° ; carbonic anhydride, mixed with a little carbonic oxide, was given off in abundance, and an acid watery

liquid distilled over. The oil-bath was kept at 200° until all evolution of gas had ceased, when the flask was removed from the bath and heated over a small flame. Nothing came over below 210° , but between this and 215° a yellow oil distilled over. When this was all over, there remained in the flask nothing but a black coaly residue.

I. *The Watery Distillate*.—This was neutralised with potassium carbonate and re-distilled. It commenced boiling below 70° , and the temperature gradually rose until it reached 100° , where it remained stationary. When about two-thirds of the liquid had passed over, the distillation was stopped, and the solution of potassium salt remaining in the flask was poured into a dish and evaporated to dryness. The quantity of salt obtained was very small, and, from its reaction with sulphuric acid and alcohol, appeared to be potassium acetate. The distillate was saturated with potassium carbonate, which caused a small layer of liquid, smelling of methylic alcohol, to separate. This was separated, dried, and distilled; it began to come over at 68° , and fractions were collected between this and 75° , 75 — 80° , 90 — 99° . There was, however, not enough of either fraction to examine. They all smelt more or less alcoholic, and were all inflammable.

II. *The Yellow Oil*.—This oil, boiling between 210 — 215° , was re-distilled; it came over between the same limits, and, from its boiling point and appearance was apparently citraconic anhydride. In order to prove this, it was dissolved in water and converted into salts. At the same time, some citraconic acid, which Professor Wislicenus kindly gave me, was taken and also converted into salts, so that the two might be compared. The following salts were prepared and analysed:—

Silver Salt.—Prepared from both by addition of silver nitrate to neutral solution of acid. In both cases a white precipitate was formed, which dissolved on boiling, and crystallised from the mother-liquor in star-like clusters of needles. When dried and analysed, the following results were obtained:—

I. Salt from acid from distillation:—

·1173 gram salt gave ·0745 gram CO_2 , ·0170 gram OH_2 and ·0713 Ag.

II. Salt from citraconic acid:—

·1312 gram gave ·0832 CO_2 , ·0190 gram OH_2 , and ·0797 gram Ag.

	Calculated for		Found.	
	$(\text{C}_5\text{H}_4\text{Ag}_2\text{O}_4)_2 + \text{OH}_2$		I.	II.
C_{10}	120	16·99	17·32	17·29
H_{10}	10	1·41	1·61	1·61
Ag_4	432	61·19	60·78	60·75
O_9	144	20·39	—	—
	<hr/>	<hr/>		
	706	99·98		

Lead Salt.—Prepared by precipitating a neutral salt with neutral

lead acetate. The precipitate obtained becomes granular on boiling with another liquor. When collected and dried, it gave the following results :—

I. Salt from acid from distillation—

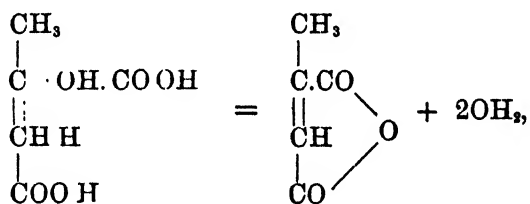
·2262 gram salt gave on combustion ·1455 gram CO_2 , ·0290 gram OH_2 , and ·1507 PbO .

II. Salt from citraconic acid—

·2380 gram gave ·1513 CO_2 , ·0288 gram OH_2 , and ·1645 gram PbO .

Calculated for $\text{C}_5\text{H}_4\text{PbO}_4$.			Found.	
			I.	II.
C_5	60	17·91	17·54	17·83
H_4	4	1·19	1·42	1·34
Pb	207	61·79	61·84	61·40
O_4	64	19·10	—	—
	<hr/>	<hr/>		
	335	99·99		

The identity of these salts, coupled with the boiling point, proves the yellow oil to have been citraconic anhydride. The principal reaction was therefore undoubtedly the following :—

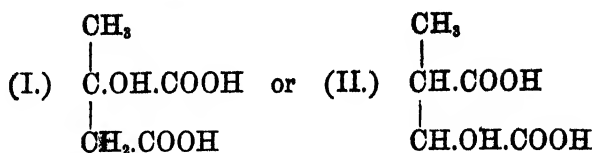


whilst a second reaction went on, which resulted in the formation of carbonic anhydride, carbonic oxide, acetic acid, and some of the lower alcohols, probably methylic, ethylic, and isopropyllic.

Remarks on the Constitution of some of the Isomerides of α -Methyl-hydroxysuccinic Acid.

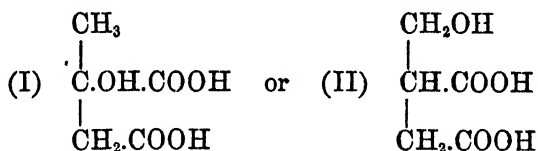
Of the constitutional formulæ of the five known acids of the general formula $\text{C}_5\text{H}_8\text{O}_6$, very little is known. I think, however, that knowing the constitution of the foregoing acid, we may fix with tolerable certainty the constitution of at least two of the previously known acids.

Citramalic acid, prepared by Carius (*Annalen*, 129, 159) by the action of hypochlorous acid upon citraconic acid, and reduction of the resulting monochlorocitramalic acid with zinc and hydrochloric acid, may have either of the two following formulæ :—

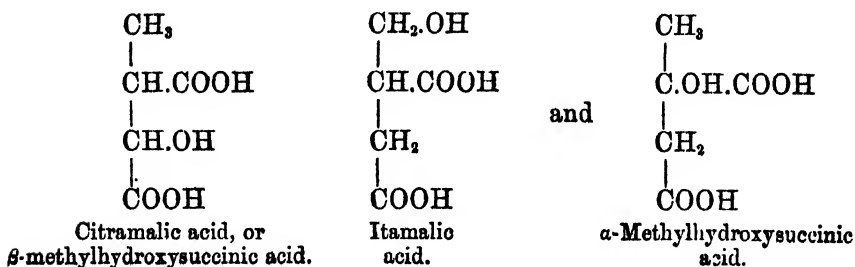


It is evident that the first of these formulæ is identical with the formula of the acid described in the preceding pages, and therefore the two acids should exhibit the same properties; but, on the contrary, they are totally different, citramalic acid being an uncrystallisable syrup which may be obtained by long standing in a vacuum as an amorphous, transparent mass, whilst α -methylhydroxysuccinic acid is easily obtained in well-defined crystals. The salts of the two acids are also entirely different. This would seem to point to the second of the above formulæ as being the correct one for citramalic acid.

Itamalic acid which Swarts (*Zeitsch. Chem.*, 1867, 646) prepared by the action of hydrobromic acid upon itaconic acid, and decomposition of the resulting itamonobromopyrotartaric acid by boiling with water or alkalis, may also have either of two following formulæ:—



But the first of these is identical both with the first of citramalic acid and also with that of α -methylhydroxysuccinic acid, whilst the acid itself differs from both in its properties, forming long deliquescent needles which melt at 60—65°, and giving salts different from those of the other two acids. This would again point to the second as being the correct formula. The formulæ for these three acids would then be:—



III.—Contributions to the History of Putrefaction. Part I.

By C. T. KINGZETT.

It appears to be now well established that matters of animal and vegetable origin present no inherent tendency to pass into a state of putrefactive decomposition. In other words, putrefaction is the expression by which is indicated a number of specific changes induced in certain bodies by causes extraneous to the substances themselves.

For the greater part of existing knowledge of this subject, we are indebted to the researches of Pasteur (*Compt. rend.*, **56**, 1189; *Jahresb. f. Chem.*, 1863, 579), who in 1863 defined putrefaction as a fermentative process induced and sustained by animal ferments of the genus *Vibrio*. This definition received confirmation from Traube and Gscheidlen (*Dingl. polyt. J.*, **222**, 352; *Chem. Soc. J.* [2], **12**, 997), among others, in 1874, and still more recently from the very interesting and well known experiments of Professor Lister.

It has been substantiated, then, that just as any kind of fermentation is an instance of a biological reaction manifesting itself as the result of a special force residing in organisms, or, in other words, as "fermentation is essentially a correlative phenomenon of a vital act, beginning and ending with it,"* so also is putrefaction such another instance of a biological reaction, or such another correlative phenomenon of a vital act. Both in fermentation proper and in putrefaction there is organisation, development, and multiplication of the living agents.

It is probable also that, although certain kinds of fermentation seem to depend upon specific unvarying organisms, yet in a modified form fermentation can also be induced in the same medium by different ferments or organisms, just as a number of hydrating agents may cause the same order of decomposition in certain chemical substances, the only difference being in the specific nature of the acting agents and the resulting products, or some of them.

Pasteur recognises two kinds of putrefaction, viz., one in which the ferment (as for instance the butyric ferment) produces the change without the aid of oxygen, and that in which oxygen is also essential in promoting such change.

But however this may be, it is certain that mere temporary exposure to the air is sufficient in the vast majority of instances to introduce into any putrescible solution the agencies of putrefactive change.

* See Schützenberger's Work on Fermentation (King and Co.), p. 39.

Under this view of things, when a putrescible solution is exposed to the air, there forms on the surface a film of bacteria, mucors, and mucidines, which are supposed to exclude and absorb oxygen, preventing it from penetrating into the liquid. Under the film in the liquid, vibriones multiply and split up the albuminous substances into simpler products, while the bacteria and the mucors excite the slow combustion of these latter into ultimate products. This is M. Pasteur's view of the changes constituting putrefaction, and it should be particularly observed that vibriones cannot endure the presence of oxygen; their function is the institution of initial change, which is completed by the bacteria and the mucors.*

"It follows from what has been said, that contact of air is by no means necessary for the development of putrefaction. On the contrary, if the oxygen dissolved in a putrescible liquid was not at once removed by the action of special organisms, putrefaction would not take place; the oxygen would destroy the vibrios which would try to develop at first."†

As regards the first products of putretactive change, so far as is known, they resemble those, or at least are identical in some measure with those, obtained by subjecting albuminoïds to chemical decomposition by hydrating agents such as dilute sulphuric acid and baryta-water. This kind of decomposition has been specially studied by Schützenberger. The ultimate products of putrefactive change would seem to result from the oxidation of the primary products and from certain ill-defined secondary influences.

Under these circumstances one would naturally expect that a substance allowed to undergo putrid fermentation without oxidation, would more readily undergo chemical oxidation than the original integral mass, and hence that the oxygen-absorbing capacity of a substance would progress increasingly with such putrefactive decomposition. It thus occurred to me some time ago that advantage might be taken of this inference to compare quantitatively the prophylactic energies of various substances by determining the oxygen-absorbing capacities of organic solutions or mixtures from time to time as they passed into putrefaction, and comparing these with the oxygen capacities of similar solutions protected during the same periods by so-called antiseptics.

Accordingly, after considerable unavoidable delay, I commenced the experiments, some of which I have now the honour of submitting to the Chemical Society.

* *Compt. rend.*, June, 1863, and Schützenberger on Fermentation (King and Co.), pp. 209—227.

† Page 219 of Schützenberger's treatise.

I have made a large number of experiments of this kind, but do not propose to publish the results on this occasion. It may be remarked that the investigation presents great difficulties, and it is only from a very large series of observations that any sound inference can be made. The problem would lose nearly all its difficulties if all antiseptics exercised the same kind of influence, say for instance the strengthening of the combinations, to break down which constitutes the function of vibriones. But this is not the case, and moreover most of the antiseptic substances tested, react upon the potassic permanganate in a chemical manner of their own. Hence the difficulties of the investigation which I am carrying on. Some of the experiments which I have made, however, seem to have an important bearing upon what Dr. Tidy describes as the "oxygen process" of water analysis, and I shall only preface the description of these experiments by stating that I was not led to the subject by any spirit of criticism, much less of hostile criticism, but purely incidentally.

There is a wide-spread opinion that in the putrid state a substance is capable of absorbing much more oxygen, or to put it in another way, of decomposing much more potassic permanganate than in the fresh state, and indeed it appears to me that the "oxygen process" of water analysis as recently described by Tidy (*Chem. Soc. J.*, 194, 80, specially) largely depends upon this assumption: for he observes, "At any rate it undoubtedly furnishes us with exact information as to the relative quantities of putrescent and easily oxidisable matter, and of non-putrescent or less easily oxidisable matters, present in the water." I shall show presently that this is not clear, and it appears to me that the oxygen process is liable to mislead chemists in interpreting their results, if we are to believe that the more pernicious organic matters are those which are in a putrescent condition. For it will be seen that a water may contain at one time organic matters in a non-putrescent condition, and that when these same matters shall have become pernicious, the water will absorb far less oxygen than originally!

Experiment 1 (August 14th, 1879).—A dilute solution of white of egg was made, filtered from membranous matter, and found to contain 1.588 per cent. albumin dried at 100° C. Of this I took 5 c.c., added 90 c.c. of distilled water, then 5 c.c. of dilute sulphuric acid (1 : 3), and lastly 20 c.c. of a standard solution of potassic permanganate (1 c.c. = .001334 gram oxygen). The mixture was allowed to stand one hour, and the unused permanganate was then determined by estimating its equivalent of iodine with a standard solution of sodic thiosulphate in the usual way (1 c.c. = .000667 gram oxygen or $\frac{1}{2}$ c.c. standard permanganate).

In this manner I ascertained that the albumin operated upon used

up during the hour 6 c.c. $\text{KMnO}_4 = 0.008004$ gram oxygen. This then I call the "initial oxygen-absorbing capacity." 45 c.c. of the same albumin solution was now placed in a stoppered bottle of about 100 c.c. capacity, and at the periods shown below the oxygen-absorbing capacity was again determined upon different portions, but under exactly identical conditions with the results also shown.

Oxygen capacity at start	After 24 hours.	After 120 hours.	After 1104 hours.
0.008004	0.008671	0.0076038	0.00667
After 1176 hours.	After 1440 hours.	After 1534 hours.	
0.0062031	0.0058696	0.0054694	

The solution began to stink after about 150 hours' standing, and henceforth it grew worse, being ultimately of a glutinous, stringy consistence, and smelling strongly of cheese, having entirely lost its purely putrefactive odour.

Experiment 2 (August 27, 1879).—A pound of raw beefsteak was digested with about 400 c.c. of water at 50°C . for two hours, filtered after cooling, and allowed to stand over night. Next morning it was already slightly putrid to the smell.

The initial oxygen-absorbing capacity was determined, using 5 c.c. of the extract, diluted with 100 c.c. of water, adding 5 c.c. of 1 : 3 H_2SO_4 and 20 c.c. KMnO_4 solution. It absorbed 0.008671 gram oxygen.

60 c.c. of the extract was now placed in a stoppered bottle of 80 c.c. capacity, and another similar bottle was entirely filled with the extract, so that it was not exposed to the air. The oxygen capacities of these two solutions were then determined at the periods and with the results here following:—

A. Partially filled Bottle.

Initial.	24 hours.	72 hours.	144 hours.	168 hours.	
0.008671	0.0089378	0.0081374	0.0081374	0.008004	
648 hours.	672 hours.	792 hours.	840 hours.	1128 hours.	1224 hours.
0.007337	—	0.006003	0.005336	0.0050692	0.0042688

B. Entirely filled Bottle.

Initial.	24 hours.	72 hours.	144 hours.	168 hours.	
0.008671	—	—	—	0.0089378	
648 hours.	672 hours.	792 hours.	840 hours.	1128 hours.	1224 hours.
0.011339	0.0037352	0.0034684	0.0034684	—	—

After 48 hours both bottles were maintained at a temperature of 40° for three hours to hasten putrefaction.

In A the putrefactive odour was unbearable before heating to this temperature, but, curiously enough, when examined after 72 hours it smelt quite sweet. It again stank at the 144 hours' examination, and the odour grew worse and worse, a deposit* occurring gradually, and much gas being evolved on agitation. Finally, the solution became quite colourless, or nearly so, all the colour being in the deposit. At the 1128 hours' examination it was perfectly sweet to smell, emitting only a meaty odour; so also at 1224 hours.

B, when first opened after 168 hours, was found to be terribly putrid, and of course after this date and up to 648 hours it was in contact with 5 c.c. of air, and after each examination the quantity of air was increased by 5 c.c. (the measure of fluid removed). As regards appearances and odour, it followed the course of A, so far as observed.

Experiment 3 (October 1, 1879).—In this experiment I took a beef-steak in which the process of putrefaction had already commenced; a piece of fresh herring in a similar condition, and the piece of a cabbage, and made an infusion at 40°, cooled and filtered it. A small stoppered bottle was then entirely filled with a quantity of this solution, and a further quantity of the same solution was placed in a corked bottle containing about 400 c.c. of air. The method of proceeding was as in the last experiment.

A. Extract in full Bottle.

Initial oxygen capacity.	After 24 hours.	After 336 hours.	After 432 hours.
0·0058696	—	0·0034684	0·00314824
After 840 hours.	After 1032 hours.	After 1128 hours.	After 1224 hours.
0·00490912	0·00410872	0·004005	0·0041385
After 1776 hours.			
0·0041408			

B. Extract exposed to Air from the start.

Initial oxygen capacity.	After 24 hours.	After 336 hours.	After 432 hours.
0·0058696	·0050692	0·0034684	0·00314824
After 840 hours.		After 1032 hours.	
0·00442888		0·0034684	

On October 13, that is to say, after 336 hours, and when putrefaction was in full work, 22·5 c.c. of the extract in Bottle A was placed in contact with 55 c.c. of air over mercury. After five days the volume

* This deposit, which occurred in all the fluids which were allowed to pass into putrefaction, was of a silty nature, and in no way interfered with the determination of the oxygen-capacities, since by agitation of the fluids it could be equally disseminated throughout the mass. This was proved by making (in the majority of instances) duplicate experiments, which always yielded the same results.

of gas in tube measured 59 c.c. A little caustic potash was now introduced, and this absorbed 4 c.c. of gas, leaving, therefore, the original volume unabsorbed. I do not attach much importance to this experiment; it was quite of a preliminary nature, and perhaps, after all, oxygen had been absorbed from the air, and an equal volume of other gas (hydrogen or nitrogen) unabsorbable by potash, set free. Be this, however, as it may, it would seem from the comparative experiments, A and B, that this one instance of putrefaction in no way depended upon the contact of air *per se*, and may, indeed, proceed independently of it.

The putrefaction in A and B proceeded rapidly, the solutions keeping their red colour, which even seemed to intensify for some time. On examination at the 336 hours both were horrible to smell, and had largely deposited; both evolved much gas on agitation. The appearance was much the same after 432 hours. Later on, the red colour of the solution disappeared, the deposit simultaneously increasing; the odour, too, changed from the recent putrefactive to a stale butyric odour. After 1032 hours, A had not lost this latter smell altogether, but B had, and emitted only the smell of some compound ammonia.

Experiment 4 (November 3, 1879).—Four or five pounds of raw lean beef was minced and macerated in pure water at about 40°. The extract contained 3 per cent. (?) solid matter, dry at 100°.

A. 200 c.c. of this extract was placed in a stoppered bottle of about 250 c.c. capacity.

B. 200 c.c. of the same extract was placed in a stoppered bottle of this exact capacity.

C. 50 was exposed to 47·5 c.c. of air over mercury.

Initial oxygen capacity of 5 c.c.	After 96 hours.	After 192 hours.	After 278 hours.	After 374 hours.	After 926 hours.
A. ·0073959	·006942	·0064614	·00631455	·006942	·00643552
B. ·0073959	—	—	·006942	·007743*	·00685776
C. ·0073959	Volume of gas in air-tube = 44·5 c.c.			·0071289	·00643552

A and B both began to stink after 48 hours from start, and both grew increasingly worse, and made a considerable whitish deposit.

Now, postponing for the moment the consideration of these results in regard to the phenomenon of putrefaction, they seem to reflect, as I have already said, upon a probable source of error in the oxygen process of water analysis. During the discussion upon Dr. Tidy's valuable paper, I pointed out that permanganate of potash, according to his own

* After this examination, a quantity of this extract was placed in a bottle of its precise measure, and at the 926 hours' stage the oxygen-capacity was found to be ·0075712.

results (this Journal, 1879, 1, 78), seems to have little influence upon gelatin in a fresh state; and since gelatin is one of a class of bodies liable to putrefactive changes, and hence liable to give rise to pernicious products, it appeared to me that the oxygen process was liable to overlook certain albuminoids, which was a serious objection. It now appears, from the experiments which I have described, that the oxygen process might not only pass a water containing such an albuminoid as good, but it might also pass a water containing pernicious products, since it is possible to obtain such a solution which will exhibit a much smaller capacity for oxygen than the original fresh solution from which it is derived.

So far as these experiments go, they confirm the fact (which has been more than once disputed*) that putrefaction can begin and proceed in the absence of oxygen (that is, as such), and in common with some researches of Nencki† they confirm the history of putrid fermentation as laid down by Pasteur.

In some of the experiments, the putrescible solution showed in the next earlier stages a tendency to undergo slightly greater oxidation than at the start; it may be because up to this time the agencies at work consisted mainly of a hydrating character; but as this proceeded and the quantity of available oxygen from without increased, other agencies initiated and carried on the oxidising influence constituting the second act of ordinary putrefaction. It would seem also that in some of the experiments the agencies at work had the power of obtaining oxygen from within the mixtures, for the quantity of oxygen available as air was in certain instances not sufficient to account for the decrease in oxygen-absorbing capacity, if we regard that decrease as due to interim oxidation. The presence of free oxygen doubtless assists the later changes.

Finally, it will be seen that in the history of putrefaction there comes a time when the activity of the agencies at work greatly diminishes, and finally almost ceases. No doubt this is due, not merely to the using up of material ready to undergo putrefactive changes, but also to the poisonous influence of the putrefactive products, when present in certain amount upon the agents themselves. This has been well shown by Crace-Calvert and Thomson‡, Nencki, and others.

Such a result is comparable with another observed in the process of alcoholic fermentation. So soon as the alcohol reaches a certain

* For instance by Gunning, in *J. pr. Chem.* [2], 19, 266.

† See paper by Nencki, *ibid.* [19], 337—358; Abstracted in *Chem. Soc. J.*, November, 1879, page 953.

‡ See a pamphlet by W. Thomson "On the Principal Agencies of Putrefaction and Decomposition." Manchester (Palmer and Howe), 1875.

amount, fermentation ceases, because the yeast cells are rendered inactive by the alcohol.*

The ground-work, however, is not sufficient to admit of much theorising, and had it not been for the interest which the results originated as to the oxygen process of water analysis, I should not have submitted the experiments in their present incomplete form.

IV.—*Notes on Manganese Dioxide.*

By C. R. ALDER WRIGHT, D.Sc. (Lond.), Lecturer on Chemistry in St. Mary's Hospital Medical School; and A. E. MENKE, Daniell's Scholar, King's College.

§ 1. *Introductory.*

THE experiments described in this paper are essentially a continuation of some observations detailed in the "Second Report on some Points in Chemical Dynamics," presented to the Society by one of us and Mr. A. P. Luff (this Journal, 1878, 1, 504), in which it was shown that pure hydrated manganese dioxide is not produced by two of the processes usually described as giving rise to that substance, viz., acting on potassium permanganate with nitric acid, and treatment of manganese chloride with sodium hypobromite; the products contained considerably less "available oxygen" than corresponds with the formula MnO_2 . These results have since been extended and confirmed by Görgen (*Compt. rend.*, 88, 796), who has observed that the products obtained by oxidising protoxide or carbonate of manganese either heated or in the cold, by treating manganate or permanganate of potassium with nitric acid, by exposing permanganic acid to spontaneous decomposition, and by electrolysing dilute solutions of manganese salts, uniformly contain less oxygen than corresponds to the dioxide. Various specimens of these products showed on titration amounts of total oxygen of from 35.2 to 36.5 per 100 parts of anhydrous substance, MnO_2 containing 36.8 parts: hence the deficiency in the "available oxygen" amounted to from 0.3 to 1.8 out of 18.4, or from $\frac{1}{8}$ to $\frac{1}{11}$ of the quantity of available oxygen in MnO_2 . These products were stable in the air or in contact with distilled

* This was shown by a large number of experiments made by Thudichum in conjunction with the author, but unfortunately the manuscript was mislaid, and so the experiments have not been published.

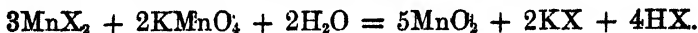
water, suffering no change even after lengthened periods of time; on treating them with potash, they *neutralised and combined with* amounts varying from 1 to 14 per cent., i.e., they acted like feeble acids, as Görgeu had previously (in 1862) found manganese dioxide to be capable of doing (*Ann. Chim. Phys.* [3], 66, 153), forming salts of the general formula $5\text{MnO}_2 \cdot \text{X}_2\text{O}$, where X is a monad. On the other hand, Görgeu has also found that the manganese dioxide produced by heating manganese nitrate to about 160° , shows little or no deficiency in oxygen, and that it does not combine with potash, exhibiting in these respects and in its physical properties a close resemblance to the natural minerals polianite and pyrolusite.

S. U. Pickering also has recently found that by dissolving manganese superoxides in large bulks of strong hydrochloric acid and diluting with water, substances are precipitated which exhibit a considerable deficiency in available oxygen as compared with MnO_2 (this Journal, 1879, *Trans.*, 654).

During the last twelve months, having had occasion to prepare a quantity of manganese dioxide for the purpose of examining the character of the curved surfaces representing the mutual relations of time, temperature, and amount of deoxidation by various reducing agents, we have examined afresh the product of the action of nitric acid on potassium permanganate, and have been surprised to find that even when the quantity of nitric acid present is very large relatively to the manganese, the substance precipitated invariably contains a not inconsiderable amount of potassium, combined so firmly as not to be in the slightest degree washed out by continued boiling with water. This circumstance has led us to examine the substances regarded as more or less pure manganese dioxide formed artificially in various ways, with a view to seeing whether potassium is similarly retained by these substances when prepared in presence of potassium compounds. Our experiments indicate that whenever potassium is present in a solution from which a manganese superoxide is precipitated, a larger or smaller quantity is invariably retained in combination in the precipitate. The same remarks appear, as far as our experiments have gone, to be equally true as regards calcium, and probably many other metals; indeed in the case of calcium, the tendency of manganese dioxide to carry down foreign metals in combination appears to be superior to its power of uniting similarly with potassium: for manganese dioxide precipitated from a solution containing a little calcium, and several times as much potassium, will frequently carry down more calcium than potassium.

The action of nitric acid on permanganate of potassium may be regarded from several points of view: thus the action may be supposed to consist in the setting free of permanganic acid, which gradually

decomposes, evolving oxygen and depositing manganese dioxide: or manganese nitrate may be supposed to be formed and to react on the undecomposed permanganate in accordance with the well-known reactions (as applied to the sulphate or chloride) on which Guyard founded his volumetric method of manganese determination:—



In either case the retention of potassium in the precipitate seems to indicate that manganese dioxide (the *acide manganoux* of Görgeu) is sufficiently acid in its character to displace nitric acid from nitrates. It is, however, difficult to see why the precipitate thrown down should exhibit a deficiency in oxygen, for being formed in presence of excess of permanganate, it should contain all the manganese as dioxide, Görgeu having stated in 1862 that when a manganous salt is added to excess of permanganate, the precipitate has the composition of hydrated MnO_2 , although a "manganite of manganese," $5\text{MnO}_2 \cdot \text{MnO}$ (or Mn_6O_{11} , exhibiting a deficiency of one-sixth of the available oxygen in MnO_2), is obtained when the permanganate is added to excess of the manganese salt (*Ann. Chim. Phys.* [3], 66, 153). Guyard subsequently stated, whilst describing his volumetric method (*Bull. Soc. Chim.* 1864, 1, 89), that the temperature of the solution influences the nature of the precipitate. At 80° a precipitate of hydrated MnO_2 is thrown down; at lower temperatures oxides exhibiting a deficiency of oxygen are obtained, corresponding with the formulæ; $4\text{MnO} \cdot \text{Mn}_2\text{O}_7$, and $5\text{MnO} \cdot \text{Mn}_2\text{O}_7$ (or Mn_6O_{11} , and Mn_7O_{12}), manganese dioxide prepared in this way being viewed by Guyard as a basic permanganate of manganese, $3\text{MnO} \cdot \text{Mn}_2\text{O}_7$, and these compounds as yet more basic analogous substances. Guyard represents the precipitate as containing the elements of the hydrate $\text{MnO}_2 \cdot \text{H}_2\text{O}$; Rammelsberg, however (*Ber.*, 1875, 233), represents the substance formed by acting on potassium permanganate solution with strong sulphuric acid, and then adding water, as $3\text{MnO}_2 \cdot 2\text{H}_2\text{O}$,* and this formulæ is also applied by Morawski and Stingl to the substance examined by them some months ago, obtained by adding manganous chloride to potassium permanganate solution and drying over sulphuric acid (*J. pr. Chem.* [2], 18, 78).

No one of these observers† appears to have noticed the presence of

* Rammelsberg gives the percentages $\text{Mn} = 55.56$ $\text{O} = 16.16$ calculated for the formula, 3MnO_2 , $2\text{H}_2\text{O}$, and $\text{Mn} = 55.48$ $\text{O} = 15.63$ as those found, thus exhibiting a slight deficiency in oxygen to the amount of $\frac{16.16 - 15.63}{16.16} = \frac{1}{32}$ part: doubtless, however, the manganese was over-estimated, as potash is carried down the precipitate. *Vide* § 4.

† Since the majority of our experiments were made, a paper has appeared by J. Volhard (*Annalen*, September, 1879, 198, 318), in which the author states that the manganese dioxide precipitate obtained by adding potassium permanganate to

considerable amounts of potassium in these products (several per cents. of K_2O). Morawski and Stingl indicate in one part of their paper that the product obtained by the action of potassium permanganate on manganese chloride is free from potassium, for they give the analytical numbers 56.0 per cent. of Mn, and 1.33 of H (calculated for $3MnO.2H_2O$, $Mn = 55.56$ $H = 1.34$). Subsequently, however, they state that traces of potassium are apparently carried down with the precipitate, as the filtrate contains rather more hydrochloric acid, and rather less potassium than corresponds to the above equation; they indicate the amount, however, as being at most only a few tenths per cent., inasmuch as they state that on treating this precipitate with potassium carbonate solution, an amount of potassium was withdrawn from the solution to the extent of 9.17 and 9.23 per cent., the compound $Mn_4KH_3O_{10}$ (or $8MnO_2.K_2O.3H_2O$) being produced; the calculated amount for the transformation of $3MnO_2.2H_2O$ into this compound is 9.87 per cent. This ultimate compound, $Mn_4KH_3O_{10}$, they state is formed whenever potassium permanganate acts in a neutral solution (originally) upon various organic substances, such as potassium thiocyanate, alcohol, glycerin, oxalic acid, &c. On repeating their experiments, as described below, we have obtained entirely different results, the alleged definite substance, $Mn_4KH_3O_{10}$, not having been produced in any one instance examined.

§ 2. *Manganese Dioxide prepared from Potassium Permanganate by Nitric Acid.*

A concentrated solution of potassium permanganate (filtered warm through glass wool) was acidulated with about one-fifth of its bulk of strong nitric acid, so that the resulting liquid contained at least 25 per cent. by weight of HNO_3 , and kept on the water-bath for some time until most, but by no means all, of the permanganate was destroyed; the heavy black precipitate was washed several times by decantation, and finally on a glass wool pump-filter, until every trace of acid was absent from the filtrate. The product was then dried over sulphuric acid for several days; when dry to the touch, the clots were pulverised by light pressure, and the whole left over sulphuric acid for some months. Portions taken out after 1, 3, and 5 months' standing over sulphuric acid, were analysed with the following results. The available oxygen was determined by boiling with hydrochloric acid, receiving the evolved chlorine in potassium iodide solution, and titrating with an excess of sodium thiosulphate, going back with a decinormal iodine solution,

manganese sulphate contains combined potassium, unless the solution is strongly acidulated with nitric acid, in which case not more than traces are present in the precipitate. Our results do not agree with his (*vide infra*) in this latter respect (*vide* §7).

against which the thiosulphate was checked. In some cases the substance was boiled with acid ferrous sulphate in excess, and the excess determined by a standard potassium dichromate solution, against which the ferrous sulphate was checked. Numerous experiments showed perfect identity between the average results of the two processes when perfectly pure dichromate and carefully standardised solutions are employed (the iodine being standardised with specially prepared pure arsenic trioxide); only a trace of iodine was generally liberated on distilling the hydrochloric acid used into potassium iodide in a blank experiment; this amount was always subtracted (with some samples of acid and iodide this correction is very appreciable). The water expelled on ignition was determined in two ways: firstly, by heating in a current of dry air, and collecting the expelled water in a CaCl_2 tube; secondly, by igniting weighed amounts, and determining the loss of weight, and the available oxygen in the residue. Subtracting this latter from the original available oxygen, the oxygen expelled was known; and subtracting this from the loss on igniting, the water expelled was known. The average results by the two processes coincided perfectly. It was found that practically the whole of the water present was expelled on ignition, the residue left on igniting several grams in a current of dry air in a large platinum boat, never giving more than a very few milligrams of additional moisture on withdrawing the boat whilst still hot, adding to its contents several times their weight of recently fused, not completely cooled potassium dichromate, and heating again to fusion of the whole mass. Minute quantities of water were, however, thus obtained,* apparently indicating that on ignition a portion of the potash present became converted into KOH. This was corroborated by the circumstance that on treating with water the ignited substance (not fused with potassium dichromate) sensible quantities of potash were dissolved out, forming a highly alkaline solution; more than half of the potassium present, however, was usually still retained in a form of combination incapable of being dissolved out by boiling water.

After 1 Month.

			Mean.
Available oxygen	15.78	15.89	15.84
Water	—	—	5.60
Manganese monoxide and potash ..	—	—	78.67
			<hr/> 100.11

* Morawski and Stingl state (*loc. cit.*, *supra*) that the same amount of water is expelled from a hydrated manganese dioxide containing potash, by simple ignition as by fusion with potassium dichromate. Our experiments show that this result is only approximately true; the residue left on ignition in a current of dry air until

After 3 Months.

						Mean.
Available oxygen	15.80	15.86	15.96	16.03	—	15.91
Water	5.31	5.14	5.01	4.93	4.88	5.05
Manganese monoxide and potash	79.24	79.04	78.83	78.72	—	78.96
						<hr/> 99.92

After 5 Months.

Available oxygen	15.93	16.02	16.05	16.16	16.04	
Manganese monoxide and potash	79.54	79.34	—	—	79.44	
Water (by difference)					4.52	
					<hr/> 100.00	

From these numbers it is evident that a very slight loss of water, but no loss of oxygen, attended the prolonged drying over sulphuric acid; the experiments with other samples of hydrated manganese dioxide described below confirm these results, indicating that no loss of oxygen whatever takes place, either during the first drying of a moist precipitate over sulphuric acid, or subsequently, but that a continual progressive loss of water takes place on long standing over sulphuric acid; when a certain amount of water is thus lost (varying with the mode of preparation) the rate of loss becomes very small, barely appreciable amounts being lost in several weeks.

The amounts of manganese monoxide and potash severally present in the sample dried for three months were carefully determined in several ways, viz., heating with hydrochloric acid (or pure sulphuric acid), evaporation to expel the greater part of the excess of acid, treating with pure yellow ammonium sulphide (specially prepared and free from alkalis), and converting the manganese sulphide into MnSO_4 , by dissolving in pure hydrochloric acid, evaporating to dryness with pure sulphuric acid, and gently igniting at a dull red heat; the filtrate was evaporated to dryness in a platinum vessel, and the residue ignited with sulphuric acid, and the potash weighed as K_2SO_4 . In some cases the weight thus obtained was checked by conversion into potassium platinochloride; it was found that if a glass or porcelain evaporating vessel were used, the potassium sulphate obtained was contaminated with lime, silica, alumina, and alkalis derived from the vessel; the same vessels hardly parted with a trace of corroded matter

no further traces of moisture were yielded to a CaCl_2 tube, invariably yielded a little moisture on adding to the still hot substance fused not quite cooled potassium dichromate, and heating again to fusion of the mass, i.e., of the potassium dichromate. The amount of additional moisture thus obtained never exceeded 0.3 per cent., however, and averaged only about 0.2 per cent. with the substances examined.

on evaporating down in them even strong hydrochloric acid solution. Another method tried was solution in hydrochloric acid, evaporation to dryness, heating finally to fusion in a crucible with a perforated lid through which a stream of hydrochloric acid gas was passed in, weighing the residual mixed chlorides, and then separating them by ammonium sulphide as before. It was found very difficult to avoid loss of manganese by volatilisation of the chloride in this way; direct experiments showed that $MnCl_2$ can be readily sublimed in a current of hydrochloric acid gas on ignition for some short time, and that the escaping gases when passed into water give an acid solution, from which a perceptible residue of manganese chloride can be obtained on evaporation to dryness on the water-bath. A third method consisted of prolonged ignition in a boat, in a current of hydrogen. At first potash sublimed in the fore part of the tube, and for some hours the substance gradually lost weight, even after the manganese was wholly reduced to green oxide; but after some 12 or 14 hours a constant weight was attained, and the residual MnO , although usually just alkaline to moist test-paper, contained only just discernible traces of potassium.* In this way the following numbers were obtained:—

	MnO.	K ₂ O.
By sulphuric acid method (weighed as sulphates)	$\left\{ \begin{array}{l} 75.51 \\ 75.51 \end{array} \right.$	$\left\{ \begin{array}{l} 3.60 \\ 3.36 \end{array} \right.$
By hydrochloric acid method (weighed as chlorides)	75.18	3.42
By ignition in hydrogen	75.37	—
	75.24	—
	75.20	—
Average	<u>75.33</u>	<u>3.46</u>

The sum of the MnO and K_2O thus found is 78.79, whilst the amount of “manganese monoxide and potash” found as above described as being left on ignition (after subtracting the “available oxygen” also left) was 78.96: whence it would seem that 0.17 per cent. of water was retained by the ignited substance in the form of KOH . This quantity sensibly accords with the amounts of moisture obtained as above described, on reheating the ignited substance with

* It was found that the green manganese monoxide thus obtained, when free from potash, did not spontaneously oxidise in the air; but if a minute quantity of potash were present, the substance usually took up oxygen, on standing in the air, becoming covered with a brown or black film: the spontaneous absorption of oxygen noticed by Wright and Luff (this Journal, 1878, 1, 526), was doubtless due to the presence of small quantities of potash in the specimens observed to undergo this change, which were at the time noticed to behave differently from pure manganese monoxide prepared by long-continued ignition in hydrogen.

a large excess of potassium dichromate; in three experiments the amounts of moisture thus obtained were 0.19, 0.17, and 0.30 per cent.; average 0.22; so that the total quantity of water present was $5.05 + 0.22 = 5.27$ per cent.

The percentages of MnO, K₂O, O, and H₂O, thus finally found correspond pretty closely with those required for the formula—



	Calculated.	Found.
MnO	75.45	75.33
O.....	15.83	15.91
K ₂ O	3.45	3.46
H ₂ O	5.27	5.27
	<hr/> 100.00	<hr/> 99.97

From this it is evident, firstly, that the water in this specimen of hydrated manganese dioxide corresponded neither with Rammelsberg's formula, $3\text{MnO}_2.2\text{H}_2\text{O}$, nor with Guyard's, $\text{MnO}_2.\text{H}_2\text{O}$, but represented a much smaller amount of hydration, which, moreover, appeared to be not constant, becoming slightly but sensibly reduced on further long standing over sulphuric acid; and, secondly, that the "available oxygen" present showed a deficiency, as compared with that in MnO_2 , of about 2 parts in 29, or between 6 and 7 per cent.

(more exactly $\frac{22.53 - 21.12}{22.53} = 6.26$ per cent., the available oxygen

present per 100 of MnO being $\frac{15.91}{75.33} \times 100$ in the sample examined,

and $\frac{16}{71} \times 100$ in MnO_2 , or respectively 21.12 and 22.53).

Another specimen of manganese dioxide was prepared in the same way. Either from a difference of temperature during the precipitation, or from some other unexplained cause, however, a considerably larger quantity of water was retained after drying over sulphuric acid for two months. By analysis as before, the following average percentages were obtained, indicating a composition pretty close to that of the preceding sample, saving as regards the combined water, agreeing fairly with the formula $34\text{MnO.O}_{32}\text{.K}_2\text{O.22H}_2\text{O}$:—

	Calculated.	Found (average).
MnO	70.67	70.68
O	14.99	14.91
K ₂ O	2.75	2.80
H ₂ O (expelled on ignition) ..	11.59	11.56
	<hr/> 100.00	<hr/> 99.95

The deficiency of oxygen in this specimen (as compared with that in MnO_2) is almost identical with that in the previous one; for the oxygen per 100 of $\text{MnO} = \frac{14.91}{70.68} \times 100 = 21.09$: whence $\frac{22.53 - 21.09}{22.53} = 6.39$ per cent., is the deficiency in oxygen in this specimen, 6.26 being that found in the former one. The amount of water retained after two months is however more than double that found in the former specimen. As in that case, this amount was not constant, for on further standing over sulphuric acid more water was lost; thus, after six weeks more (making fifteen weeks in all) the second specimen contained only 9.54 per cent. of water.

In order to see whether the deficiency in oxygen in these samples was possibly caused by spontaneous decomposition during drying, a third specimen was prepared by adding to a hot, nearly boiling solution of permanganate twice its volume of concentrated nitric acid, so that the total liquid contained upwards of 70 per cent. of HNO_3 ; in a few minutes a large portion of the permanganate was decomposed, but by no means all. The whole was then largely diluted with water, the precipitate washed by decantation several times, finally drained on a pump-filter, and examined without drying, in order to avoid the possibility of any loss of oxygen during the drying. An unknown quantity of the moist substance was heated with hydrochloric acid, and the evolved chlorine titrated; the residual chlorides were evaporated down with sulphuric acid to convert them into sulphates, and the potash separated from the manganese by ammonium sulphide as above described. In this way numbers were finally obtained for the weights of MnO , K_2O , and O present, yielding the following percentages relatively to their sum, corresponding with the formula $43\text{MnO} \cdot \text{O}_{40}\text{K}_2\text{O}$.

	Calculated.	Found.
MnO	80.62	80.46
O	16.90	17.04
K_2O	2.48	2.50
	<hr/> 100.00	<hr/> 100.00

The deficiency in oxygen in this specimen was therefore almost identical with that found with the previous two specimens: for the oxygen per 100 MnO was $\frac{17.04}{80.46} \times 100 = 21.18$, whence the deficiency, as compared with MnO_2 , was $\frac{22.53 - 21.18}{22.53} = 5.99$ per cent., the other two specimens giving respectively 6.26 and 6.39 per cent. deficiency. The amount of potassium retained in combination in this specimen, however, is perceptibly smaller than the quantity found in

either of the other two samples, doubtless owing to the effect of the larger proportion of nitric acid used.

Some observations were made on the loss of moisture and oxygen experienced by the first two samples of substance, on heating in a slow current of dry purified air for various periods to 100° , and also to 210° (in a bath of naphthalene vapour). The loss of oxygen was determined by carefully titrating the substance before and after the exposure, the loss of weight being also determined; by subtracting from the loss of weight the loss of oxygen found by the difference between the titrations (reckoned in each case per 100 parts of the substance originally employed), the amount of water expelled was known. In some instances this amount was checked by igniting the dried substance in a stream of dry air, and collecting the expelled water in a CaCl_2 tube. The following numbers were obtained at 210° as the averages of several determinations in each instance:—

	Sample I (dried 3 months over sulphuric acid.)				Sample II.	
	3	8	9	15	9	25
Time in hours						
Oxygen lost (per 100 of original substance) ..	0·25	0·29	0·30	0·47	0·23	0·43
Water lost at 210°	4·33	4·03	4·20	4·33	9·92	9·96
Water expelled from residue on ignition	0·87	—	0·89	—	—	1·77
Total water	5·20	—	5·09	—	—	11·73

At 100° the following numbers were obtained as averages:—

	Sample I.			Sample II.	
	9	30	47	9	15
Time in hours					
Oxygen lost (per 100 of original substance)....	—	0·10	0·03	—	Nil (a gain of 0·02 was actually determined).
Water lost at 100°	1·87	2·23	2·26	7·13	7·30
Water expelled from residue on ignition	3·44	—	—	—	4·57
Total water	5·31	—	—	—	11·87

The total water capable of expulsion by heat deduced from the previous analyses was 5·05 for Sample I, and 11·56 for Sample II.

From these numbers it is evident that whilst the loss of oxygen

experienced at 100° is no greater than the experimental errors of analysis, at 210° a slight but perceptible evolution of oxygen appears to take place. The amounts of water retained at the ordinary temperature, at 100° and at 200° , also appear to be very variable, the substance retaining the most at any one temperature also retaining the most at any other temperature. Some specimens (such as those described in the 2nd Report) appear to become practically anhydrous at 200° in a few hours, whilst the above specimens retained from 0.87 to 1.77 per cent.

S. U. Pickering states (*loc. cit.*, *supra*) that from 3 to 6 per cent. of water was retained by the samples examined by him after drying at 200° .

§ 3. *Manganese Dioxide from Manganese Superchloride by precipitation with Water.*

In order to see if potassium is carried down by manganese when precipitated from a solution of superchloride by copious addition of water, a quantity of the substance above described prepared from potassium permanganate by the action of nitric acid (containing $\text{MnO} = 70.68$, $\text{K}_2\text{O} = 2.80$, $\text{O} = 14.91$, $\text{H}_2\text{O} = 11.56$) was dissolved in about 50 parts of concentrated hydrochloric acid, and the solution filtered through glass wool. To one half of the solution a quantity of concentrated solution of potassium nitrate was added (the amount of salt added being about treble the weight of the dioxide used), and the whole then thrown into water; after standing 24 hours the precipitate was washed by decantation, and finally on the pump-filter. The other half was precipitated by addition of water only. The substances obtained were examined whilst still wet by boiling with hydrochloric acid to determine the oxygen, and separating the manganese and potassium from the resulting chlorides as above described. The following percentages were obtained, calculated on the sums of the K_2O , MnO , and O found, corresponding respectively with the formulæ $49\text{MnO} \cdot \text{O}_{48} \cdot 2\text{K}_2\text{O}$, and $113\text{MnO} \cdot \text{O}_{108} \cdot \text{K}_2\text{O}$.

		MnO.	O.	K ₂ O.
Sample prepared with potassium nitrate	Found	78.38	17.33	4.29
	Calculated ..	78.45	17.31	4.24
Sample prepared without	Found	81.55	17.50	0.95
	Calculated ..	81.49	17.55	0.96

As indicated by the experiments of Pickering, each of these specimens contained less oxygen than corresponds to MnO_2 , the oxygen per 100 of MnO being respectively 22.11 and 21.46, corresponding to deficiencies in oxygen of 1.86 and 4.75 per cent. respectively; these

numbers, moreover, are in harmony with the experiments subsequently described (§ 7), the deficiency in oxygen being least in the sample containing the most potash. The potassium present per 100 of MnO is greater in the first sample than in the original substance, but less in the second example:—

$$\begin{array}{lcl} \text{Original substance: } \text{K}_2\text{O per 100 MnO} & = & \frac{2.80}{70.68} \times 100 = 2.96 \\ \text{Sample prepared with KNO}_3 & , & \frac{4.29}{78.38} \times 100 = 5.47 \\ \text{,, ,, without ,, ,,} & , & \frac{0.95}{81.54} \times 100 = 1.16 \end{array}$$

whence it results that decomposition of the added potassium nitrate (or of the potassium chloride formed from it by the action of the strong hydrochloric acid) must have been produced by the manganese dioxide at the moment of its formation from the superchloride, and the potassium carried down in combination with the manganese and oxygen. In the second sample, the effect of the large quantity of acid has diminished the amount of potassium retained by the manganese, just as was observed with nitric acid previously (§ 2). It would thus seem that the distribution of the potassium in solution between the mineral acid and the precipitated manganese dioxide is regulated, amongst other things, by the relative masses of acid and manganese present (possibly also it depends on the state of dilution, temperature, &c.).

§ 4. *Manganese Dioxide prepared by the Action of Sulphuric Acid on Potassium Permanganate.*

A warm concentrated solution of potassium permanganate was treated with its own bulk of pure sulphuric acid cautiously dropped in, and the boiling hot fluid largely diluted with water. The precipitate which subsided gave the following numbers after drying for some days over sulphuric acid until apparently perfectly dry, approximately bearing out Guyard's statement that the hydrated manganese dioxide formed by precipitation contains $\text{MnO}_2 \cdot \text{H}_2\text{O}$; a notable amount of potash was, however, also present, the numbers agreeing with the formula $23\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 22\text{H}_2\text{O}$:—

	Calculated.	Found.
MnO	65.57	65.51
O	14.77	14.89
K ₂ O	3.77	3.69
H ₂ O	15.89	15.91 (by difference)
	100.00	100.00

No deficiency of oxygen at all was here perceptible, the oxygen per 100 MnO_2 found rather exceeding that due to MnO_2 (through experimental errors, doubtless); for $\frac{14.89}{65.51} \times 100 = 22.73$, whilst MnO_2 requires 22.53.

On standing over sulphuric acid at the ordinary temperature a loss of water was noticed without loss of oxygen; after another fortnight the sample contained $\text{MnO} = 67.74$, $\text{O} = 15.25$, $\text{K}_2\text{O} = 3.90$, $\text{H}_2\text{O} = 13.11$, corresponding with the formula $23\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 17\text{H}_2\text{O}$, and indicating therefore a loss of nearly one-fourth of the water. The oxygen per 100 MnO was, as before, the same as that due to MnO_2 , within the limits of experimental error; for $\frac{15.25}{67.74} \times 100 = 22.51$ (MnO_2 requires 22.53). After yet another fortnight the percentage of water was 12.77, indicating that the rate of loss of water had become greatly reduced.

From these numbers and those obtained with the specimens above described, prepared from potassium permanganate by means of nitric acid (§ 2), it would seem that the hydrated manganese dioxide thrown down by precipitation at first approximates to $\text{MnO}_2 \cdot \text{H}_2\text{O}$, and that the water is gradually lost over sulphuric acid, but not completely, a certain amount (depending, probably, on the physical state and apparently on the quantity of K_2O present, *vide* §§ 6 and 7) being retained with considerable firmness even at temperatures up to 210° .

§ 5. *Manganese Dioxide prepared by the Action of Sulphur Dioxide on Potassium Permanganate.*

A stream of washed sulphur dioxide was led into a cold solution of potassium permanganate, which was kept in large excess throughout: the brown precipitate was washed thoroughly by decantation and on the pump-filter, and then yielded the following numbers (analysed as above described whilst still wet) agreeing with the formula— $14\text{MnO} \cdot \text{O}_{12} \cdot \text{K}_2\text{O}$:—

	Calculated.	Found.
MnO	77.66	77.74
O	15.00	14.97
K_2O	7.34	7.29
	<hr/> 100.00	<hr/> 100.00

A very large deficiency in oxygen is here noticeable, the oxygen per 100 of MnO being $\frac{14.97}{77.74} \times 100 = 19.26$, whence the deficiency relatively to MnO_2 is $\frac{22.53 - 19.26}{22.53} = 14.51$ per cent.

§ 6. *Manganese Dioxide prepared by the Action of Alcohol or Glycerin on Potassium Permanganate.*

According to Morawski and Stingl (*loc. cit.*, *supra*), the brown precipitate formed when glycerin or alcohol is added to permanganate solution, and the whole gently warmed, contains the elements of the compound $8\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$, after drying at 100° . Our experiments do not confirm this. A nearly saturated cold solution of permanganate was added to glycerin dissolved in 6 or 8 parts of water, and the whole gently warmed (temperature ultimately about $30\text{--}35^\circ$). After a few minutes the whole of the permanganate was reduced: the brownish-black muddy precipitate was thoroughly washed and analysed as above described whilst still wet; two different samples, A and B, gave the following numbers, the numbers in the column headed C being obtained with a third specimen, in the preparation of which alcohol was substituted for glycerin:—

	A.	B.	C.
Available oxygen..	12.99	11.41	14.37
MnO	78.56	82.36	70.78
K ₂ O	8.45	6.23	14.85
	<hr/> 100.00	<hr/> 100.00	<hr/> 100.00

These numbers correspond respectively with the approximate formulæ, $12\text{MnO} \cdot \text{O}_9 \cdot \text{K}_2\text{O}$; $35\text{MnO} \cdot \text{O}_{22} \cdot 2\text{K}_2\text{O}$; and $20\text{MnO} \cdot \text{O}_{18} \cdot 3\text{K}_2\text{O}$, differing widely from one another and from Morawski and Stingl's formula (which becomes $8\text{MnO}_2 \cdot \text{K}_2\text{O}$ when reckoned on the anhydrous substance) not only in the presence of different quantities of potassium relatively to the manganese, but also in the manganese being associated with very much smaller quantities of oxygen than correspond to MnO_2 . After drying over sulphuric acid and finally at 100° for six hours, these three substances contained respectively 9.77, 10.21, and 9.57 per cent. of water expelled on ignition (collected in a CaCl_2 tube), thus indicating the retention at 100° of much larger quantities of water than were observed with the substances prepared by heating permanganate solution with nitric acid (§ 2). Morawski and Stingl's formula requires 6.40 per cent. of water.

According to Morawski and Stingl, the same compound, $8\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$, is produced when hydrated manganese dioxide is heated with potassium hydrate or carbonate solution, well washed, and dried at 100° . We treated with a large excess of dilute caustic potash solution the substance described in the next section, prepared by acting with hot dilute manganese sulphate solution on excess of hot potassium permanganate solution, the whole being kept in boiling water for

12 hours: after thorough washing and drying over sulphuric acid for a few days, till apparently quite dry, the following numbers were obtained agreeing with the formula, $21\text{MnO}_2.4\text{K}_2\text{O}.19\text{H}_2\text{O}$ (approximating to Görgen's formula, $5\text{MnO}_2\text{X}_2\text{O}$).

	Calculated.	Found.
MnO.....	58.59	58.51
O	13.20	13.24
K ₂ O	14.77	14.87
H ₂ O	13.44	13.38 (by difference).
	<hr/> 100.00	<hr/> 100.00

After drying at 100° for several hours, this substance retained 9.73 per cent. of water capable of expulsion on ignition; whence it would seem, as indicated also by the numbers obtained with the substances prepared by acting on permanganate with alcohol and glycerin, that the presence of much potash diminishes the ease with which water is expelled; experiments corroborative of this are also described in the next section.

§ 7. *Manganese Dioxide prepared by the Action of Potassium Permanganate on Manganese Sulphate.*

In order to test the correctness of Görgen's and Guyard's statements (*supra*) as to the amount of oxygen relatively to the manganese precipitated under different conditions, four experiments were made with the same solutions of pure manganese sulphate and potassium permanganate, each solution containing about 5 per cent. of the dissolved salt. In the first and second experiments the manganese sulphate solution was slowly poured into a considerable excess of permanganate, the solutions being both at 80—85° in the first case, and cooled down (after dissolving the salts with the aid of heat) to the ordinary temperature in the second case. The third and fourth experiments were analogous respectively to the first and second as regards temperature, but differed in that the permanganate solution was poured into a considerable excess of manganese sulphate. The precipitates were well washed by decantation, and finally on the pump-filter, and examined whilst still wet, an unknown weight being boiled with hydrochloric acid to determine the oxygen, and the manganese and potassium determined in the resulting mixed chloride solution. The following percentages were deduced from the sums of the weights of MnO, O, and K₂O thus found, corresponding respectively with the approximate formulæ:—

No. 1.....	15MnO ₂ .K ₂ O.
„ 2.....	72MnO.O ₇₁ .3K ₂ O.
„ 3.....	65MnO.O ₆₂ .2K ₂ O.
„ 4.....	66MnO.O ₆₂ .K ₂ O.

		MnO.	O.	K ₂ O.
No. 1	{ Found	76·32	17·06	6·62
	{ Calculated	76·12	17·16	6·72
" 2	{ Found	78·24	17·39	4·37
	{ Calculated	78·28	17·40	4·32
" 3	{ Found	79·62	17·14	3·24
	{ Calculated	79·64	17·12	3·24
" 4	{ Found	81·21	17·17	1·62
	{ Calculated	81·19	17·18	1·63

In the case of sample No. 1, the deficiency in oxygen is so small as to be almost within the limits of experimental error; the other samples, especially the two last, show perceptibly larger amounts of deficiency:—

		Oxygen per 100 of Mn ₂ O ₃ .	Deficiency compared with MnO ₂ .
No. 1	$\frac{17·06}{76·32} \times 100 = 22·35$	$\frac{0·18}{22·53} = 0·81$	per cent.
" 2	$\frac{17·39}{78·24} \times 100 = 22·22$	$\frac{0·31}{22·53} = 1·38$	"
" 3	$\frac{17·14}{79·62} \times 100 = 21·53$	$\frac{1·00}{22·53} = 4·44$	"
" 4	$\frac{17·17}{81·19} \times 100 = 21·15$	$\frac{1·38}{22·53} = 6·17$	"

It would thus seem that whilst the formation of such substances as the Mn₂O₃ and other oxides yet more deficient in oxygen, described by Guyard and Gorgeu did not take place in these experiments, yet the statement of Guyard that precipitation in the cold yields a substance more deficient in oxygen than one similarly prepared at about 80° is perfectly correct, specimens Nos. 2 and 4 (prepared cold) containing respectively less oxygen relatively to the MnO present than Nos. 1 and 3 (prepared at 80—85°). It is also noteworthy that the amount of combined potassium in these four specimens varies inversely with the deficiency in oxygen: in other words, the more potassium oxide is present combined with MnO₂, the less MnO is carried down similarly combined. As might be anticipated, too, more MnO is thus carried down when the MnSO₄ is in excess than when the permanganate is.

By using more dilute solutions of manganese sulphate and permanganate, keeping the latter in excess, and precipitating hot (at about 80—90°), it is possible to obtain a precipitate containing every trace of the manganese present as MnO₂ (associated with potash). Thus experiment No. 1 was repeated, employing solutions of one-tenth the strength (0·5 per cent. of each salt present). The precipitate obtained

after drying over sulphuric acid for a few days till apparently quite dry, gave numbers agreeing with the formula $11\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 0.7\text{H}_2\text{O}$, and exhibited no deficiency in oxygen:—

	Calculated.	Found (average).
MnO	66.35	65.85
O	14.95	14.94
K ₂ O	8.00	8.26
H ₂ O	10.70	10.95 (by difference).
	<hr/> 100.00	<hr/> 100.00

Oxygen per 100 MnO = $\frac{14.94}{65.85} \times 100 = 22.69$, MnO₂ requiring 22.53.

It is noteworthy that in this case the amount of potash present relatively to the manganese is greater than was the case with specimen No. 1, which exhibited a small deficiency in oxygen; the water present in this specimen was considerably below that required for the formula $\text{MnO}_2 \cdot \text{H}_2\text{O}$, but was close to that required for $3\text{MnO} \cdot 2\text{H}_2\text{O}$: the latter gives the ratio, $\frac{2\text{H}_2\text{O}}{3\text{MnO}} = \frac{36}{213} = 16.90$ per cent., whilst

there was found $\frac{10.95}{65.85} = 16.63$ per cent. So far as this particular

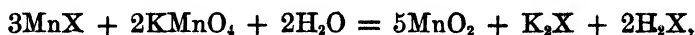
specimen is concerned, therefore, the view of Rammelsberg that hydrated manganese dioxide is $3\text{MnO}_2 \cdot 2\text{H}_2\text{O}$, would appear to be confirmed; but the previously described experiments indicate that the composition is actually variable between the limits $\text{MnO}_2 \cdot \text{H}_2\text{O}$, and something roughly approaching the anhydrous state according to the length of time that the specimen is allowed to stay over sulphuric acid: which is further confirmed by the following numbers representing the percentages of water expelled on ignition and collected in a CaCl_2 tube from the specimens Nos. 1, 2, 3, and 4 just described, each dried over sulphuric acid for one week and three weeks: Nos. 1 and 2 were coppery coloured when first examined, Nos. 3 and 4 nearly black.

Percentage of Water collected.

	Dried over H_2SO_4 1 week.	Dried 3 weeks.
No. 1	15.39	13.22
" 2	16.53	12.90
" 3	8.28	7.50
" 4	9.41	9.08

As previously indicated, § 6, the specimens containing most potash parted with water least rapidly.

It is possible to obtain complete precipitation of manganese as MnO_2 in the cold by adding zinc sulphate to the permanganate solution, and then gradually pouring in the manganese salt so that the permanganate is always in excess. Determinations made thus with known quantities of manganese furnished amounts of precipitate containing available oxygen equal to 37.5 to 37.65 per 100 MnO in the manganese salt used. Since the precipitate is formed in virtue of the reaction—



three-fifths of the manganese in the precipitate comes from the manganese salt, and two-fifths from the permanganate, wherefore the available oxygen due to the manganese was equal to 0.6×37.5 to 0.6×37.65 , or 22.50 to 22.59 per 100 MnO , MnO_2 , requiring 22.53 (*vide* § 9).

Since these experiments were made a paper by Volhard has appeared (*Annalen*, 198, 318), in which the author states that pure manganese dioxide, containing at most traces of potash, is obtainable by dissolving 10 grams of manganese sulphate in half a litre of water, adding 100 c.c. of nitric acid, sp. gr. 1.2, heating on the water-bath, adding excess of permanganate, keeping on the water-bath for an hour, and washing the precipitate at first with water acidulated with nitric acid and by decantation, and finally on the filter, and drying on bibulous paper, &c.

The foregoing experiments, however, would indicate that a greater amount of potassium is carried down in combination with the manganese dioxide than would appear from Volhard's statements. On preparing some of the product in exact accordance with his directions, thoroughly washing, and drying for a few days over sulphuric acid till apparently quite dry to the touch, the following numbers were obtained, indicated by the formula $30\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 0.17\text{H}_2\text{O}$:—

	Calculated.	Found (average).
MnO	70.76	70.65
O	15.95	16.00
K ₂ O	3.12	3.07
H ₂ O	10.17	10.28
	<hr/> 100.00	<hr/> 100.00

Ratio of MnO to available oxygen. . . 100 to 22.62.

Calculated for MnO_2 100 to 22.53.

The amount of potash in this sample relatively to the manganese was, however, notably less than was the case with either the last-described substance (prepared from 0.5 per cent. solutions of manga-

nese sulphate and potassium permanganate) or the previously described substance No. 1 (prepared from 5 per cent. solutions), doubtless owing to the influence of the added nitric acid; so that Volhard's observation that the amount of potash carried down is lessened by adding nitric acid is (as also indicated by the previously described experiments §§ 2 and 3) perfectly correct, the only error being in the actual amount of potash carried down, which is evidently much more than mere traces.

§ 8. *Manganese Superoxide prepared by the Action of Air and Caustic Potash on Manganese Chloride.*

Manganese chloride (prepared by boiling permanganate of potassium with hydrochloric acid, and evaporation nearly to dryness to expel the excess of acid) was dissolved in some 20 parts of water, and excess of caustic potash added: the whole was placed in a flask, with a wash-bottle cork and tube attached, so that by attaching an aspirator to the shorter tube a continuous current of air could be sucked through the whole, and the manganese oxidised in accordance with Weldon's well known method. After some 30 hours' treatment, a large portion of the manganese was peroxidised; the brown precipitate after thorough washing contained (reckoned as anhydrous):—

Available oxygen	10·24
Manganese oxide, MnO	87·53
K_2O	2·23
	<hr/>
	100·00

A little lime, derived from impurity in the caustic potash, was also present. These numbers are represented by the formula $52MnO \cdot O_{71} \cdot K_2O$. The great deficiency in oxygen is doubtless due to the action of the air not having been prolonged sufficiently, and being allowed to take place at the ordinary temperature. A considerable quantity of potash was permanently combined with the manganese, notwithstanding.

§ 9. *Manganese Dioxide precipitated by Bromine in presence of Potassium Acetate.*

It has long been known that manganese dioxide precipitated from an acetate solution by bromine or chlorine is apt to carry down alkalis with it, increasing its weight, so much so that in various analytical text-books (*e.g.*, Fresenius's) it is stated that the precipitate must be dissolved in acid and reprecipitated as carbonate before ignition to convert it into Mn_3O_4 . In order to see how much potassium could be carried down in presence of a very large amount of potassium salts,

some potassium permanganate was boiled with hydrochloric acid, and the solution treated with a quantity of potassium acetate, in quantity representing some 15—20 times as much potassium as there was present manganese (to avoid presence of lime the potassium acetate was made from redistilled acetic acid and calcined cream of tartar precipitated from pure nitre by tartaric acid). The whole was heated on the water-bath, and a considerable excess of bromine dissolved in strong potassium bromide solution added, so that altogether the potassium present was probably about 25 times the weight of manganese in solution. After standing on the water-bath for about an hour, the precipitate was washed by decantation and on the pump-filter, and analysed wet, as above described, with the following results in percentages of the sum of the K_2O , MnO , and O found, corresponding nearly with the formula $50MnO_2.7K_2O$.

	Calculated.	Found.
MnO	70.89	71.03
O	15.97	15.94
K_2O	13.14	13.03
	<hr/> 100.00	<hr/> 100.00

$$\text{Oxygen per 100 MnO} = \frac{15.94}{71.03} \times 100 = 22.44.$$

$$\text{Calculated for MnO}_2 = 22.53.$$

After standing over sulphuric acid for a week, this substance contained 14.18 per cent. of water, corresponding with



After three weeks the quantity was diminished to 8.90 per cent., numbers being obtained agreeing with the formula $50MnO_2.7K_2O.27H_2O$.

	Calculated.	Found.
MnO	64.61	64.73
O	14.56	14.50
K_2O	11.99	11.87
H_2O	8.84	8.90
	<hr/> 100.00	<hr/> 100.00

$$\text{Oxygen per 100 MnO} = \frac{14.50}{64.73} \times 100 = 22.40.$$

$$\text{MnO}_2 \text{ requires..} = 22.53.$$

It is hence manifest that the sample lost water on drying over sulphuric acid to considerably below the amount due to the formula $3MnO_2.2H_2O$, like most of the other samples examined; further, that

loss of oxygen accompanied the desiccation; and thirdly, that the deficiency in oxygen compared with MnO_2 was but small, viz., at most $\frac{0.13}{22.53} = 0.58$ per cent.

Other samples prepared in a similar way but in presence of much smaller quantities of potassium salts, exhibited much larger deficiencies in available oxygen, the deficiency being apparently increased if the precipitation took place at temperatures considerably below $90-100^\circ$. The largest deficiency noticed was in a specimen which gave (after standing over sulphuric acid for a few days till dry to the touch) numbers agreeing with the formula $64\text{MnO} \cdot \text{O}_{35} \cdot \text{K}_2\text{O} \cdot 63\text{H}_2\text{O}$, exhibiting a deficiency of upwards of 14 per cent., conjoined with but a small percentage of potash.

§ 10. Volumetric Determination of Manganese.

It has been shown by Kessler (*Zeits. Anal. Chem.*, 1879, 18, Part I) that by slowly adding manganese solution to hot bromine-water containing zinc chloride and sodium acetate, and finally boiling, the whole of the manganese can be thrown down as MnO_2 (associated with zinc), whilst Pattinson has simultaneously found (this Journal, 1879, 1, 365) that ferric chloride or zinc chloride will produce the same result when added to the manganese solution along with bromine-water, calcium carbonate being finally added to the hot liquid. We have repeated the experiments of these observers, both in their original forms and with modifications, and can corroborate their accuracy, with certain reservations in the latter case. Substances containing known amounts of manganese were dissolved to known volumes, and equal aliquot parts taken and examined in various ways—(a) by exactly following Kessler's directions; (b) using Pattinson's original method, employing bromine-water and ferric chloride; (c) employing Pattinson's modified method (*loc. cit.*, 371), employing zinc sulphate in lieu of ferric chloride; (d) using a simple modification of this last process, viz., adding to the somewhat acid hot solution a considerable excess of bromine-water, and then freshly precipitated zinc carbonate. In all four cases results were obtained (by washing and titrating the precipitates with ferrous sulphate and dichromate or permanganate) agreeing closely with each other and with the amount of manganese actually present, the differences between the results of the four processes not being greater than the differences between the results of repetitions by the same process. To obtain the best results we found it desirable to boil the liquid and precipitate after digesting on the water-bath for a few minutes (the precipitation being effected at a temperature as near 100° as possible), so as to expel all free bromine,

as directed by Kessler. The precipitates obtained thus by methods *a*, *c*, and *d*, contained the whole of the manganese present as MnO_2 (of course associated with zinc oxide, &c.). When the ferric chloride method was used, however, the filtrate almost invariably contained permanganate in solution, whereas this never occurred with any of the processes in which zinc was employed. We found that the best method of estimating the manganese thus contained was the comparison of its tint with an equal bulk of water coloured with measured quantities of decinormal permanganate solution; this comparison is not readily made unless the whole or almost the whole of the free bromine has been boiled off, owing to the alteration in colour produced by the bromine. Reduction by alcohol, &c., invariably gave a precipitate containing less available oxygen than corresponded to the manganese contained therein (*vide* § 6), and hence led to an under estimation of the total manganese present. We obtained good results when the solutions were so diluted that about 150 to 200 c.c. of total fluid (including bromine-water) were present for every 0.1 gram of MnO_2 precipitated, using a quantity of zinc sulphate or ferric chloride containing from 1.5 to 2 parts of metal for 1 part of MnO_2 , and sufficient bromine-water to make the supernatant fluid after precipitation moderately dark amber or sherry colour, in short, an excess of two or three times the amount of bromine actually requisite for oxidation of the manganese.

All these processes, however, are open to the objection that they require the use of bromine (or bleaching powder), and are apt to impregnate the air of the laboratory disagreeably with the vapours thereof unless worked in a fume chamber: the following modification of Guyard's permanganate process we found to give good results, and to be less troublesome as regards manipulation than any of the others. The solution, which should not contain much free acid, especially if hydrochloric acid is present, is diluted with water until it contains no more than equivalent to 0.1 gram MnO_2 in 150 or 200 c.c.; zinc sulphate to the extent of some 10 parts of crystallised salt per 1 of MnO_2 to be precipitated is then added to weak (about 0.5 per cent.) solution of permanganate, the quantity of which is somewhat more than that required to precipitate the manganese salt; this latter is then slowly poured into the permanganate (*not vice versa*) without heating and with shaking or stirring. In a few minutes most of the supernatant pink fluid can be poured off through a glass-wool filter on to which the precipitate is brought and washed: finally, the precipitate is titrated with ferrous sulphate and dichromate or permanganate; three-fifths of the manganese dioxide thus found is due to the manganese in the solution examined. To minimise sources of error, the dichromate or permanganate solution should be standardised in the

same way with a manganese solution of known strength; if the permanganate solution be hot, too high results are apt to be obtained through partial decomposition of the excess of permanganate, either by heating alone, or more probably by the action of traces of volatile organic matter in the water used for washing, dust, &c.; whilst if the zinc sulphate be omitted and the precipitation effected in the cold, too low results are obtained owing to the formation of a precipitate containing a deficiency of oxygen (§ 7). The following numbers obtained with equal bulks (50 c.c.) of one and the same manganese solution illustrate the nature of the results obtainable, similar values being obtained in numerous other analogous experiments; the numbers are given in cubic centimeters of quintinormal ferrous solution ($\frac{1}{5} \times 28$ gram Fe in the ferrous state per litre) oxidised by the manganese dioxide precipitated.

1. Precipitated by adding to <i>boiling</i> solution of permanganate.....	32·8 c.c.
2. Precipitated by adding to <i>cold</i> solution of permanganate, without ZnSO_4	32·25 „
3. Precipitated by adding to <i>cold</i> solution of permanganate, with ZnSO_4	32·65 „
4. Precipitated hot by Pattinson's original process (ferric chloride and calcium carbonate) after correction for a small quantity of permanganate formed.....	32·55 „
5. Precipitated hot by Pattinson's modified process (zinc sulphate and calcium carbonate).....	32·6 „
6. Precipitated hot by adding bromine-water and zinc carbonate	32·55 „
7. Precipitated hot by adding bromine-water and 20 parts sodium acetate to 1 of MnO_2 formed	32·1 „
8. Precipitated by exactly following Kessler's directions (bromine-water, sodium acetate, and zinc chloride used)	32·6 „

Evidently the boiling permanganate method (1) gives slightly too high a value through decomposition of the excess of permanganate, whilst the cold permanganate without ZnSO_4 (2), and the sodium acetate without ZnSO_4 (7) methods precipitate substances deficient in oxygen as shown above (§§ 7 and 9). The other methods give practically identical results; of these, No. 3 involves the least trouble and inconvenience.

§ 11. *Manganese Dioxide prepared from Manganese Nitrate by Heat.*

Pure manganese carbonate was dissolved in just sufficient dilute nitric acid, and the solution evaporated to a syrup, which was then heated to 160—165° in an air-bath for some hours. Precisely as described by Görgen, a pyrolusite-like substance was thus obtained after treatment of the product with boiling water and thorough washing: when dried in the air or over sulphuric acid for a few days, a little moisture was retained, a portion only of which was expelled on heating to 210° for several hours. The following numbers were obtained, the manganese being determined (a) by weighing as MnSO_4 , (b) by igniting and determining the "available oxygen" left in the residue, and (c) by reduction in hydrogen at a red heat.

	(a)	(b)	(c)	Mean.
MnO	80.74	80.45	80.63	— 80.61
O (by iodine process)....	18.19	18.23	18.39	— 18.23
H ₂ O by ignition and collection in a CaCl_2 tube..	1.32	1.25	1.02	0.96 1.14
				<hr/> 99.98

The oxygen per 100 of MnO found is $\frac{18.23}{80.61} \times 100 = 22.61$.

MnO₂ requires 22.53.

On heating a portion of this substance to 210° (in a naphthalene vapour-bath) in a current of dry air for four hours, a loss of weight of 0.34 per cent. only was observed, which did not increase even after nine hours. The residue thus left when ignited gave off visible quantities of water, the amount collected in a CaCl_2 tube being 0.62 per cent. No loss of oxygen whatever occurred even in nine hours: not only was the loss of weight a trifle *under* that due to the average water found ($0.34 + 0.62 = 0.96$ against 1.14 per cent.), instead of being above it, as would be the case were oxygen expelled as well as water, but further, the residue left gave on titration 18.25 of oxygen per 100 of original substance, or precisely the same amount as that found before drying.

According to Görgen, *pure* manganese dioxide is produced even if other metallic nitrates (e.g., potassium, calcium, &c., nitrates) are present in the manganese nitrate employed.

In order to see whether this substance is wholly free from potassium, a mixture of about equal weights of manganese nitrate and potassium nitrate was dissolved in water, evaporated to a thick syrup on the water-bath, and heated to 160° for several hours. The pyrolusite-like

substance obtained was crushed and well washed with hot water, and then contained (after drying in the air)—

MnO.	K ₂ O.	O.	H ₂ O (by difference).	
79.37	1.64	17.67	1.32	= 100
Oxygen per 100 MnO				= 22.27

The potash present, however, was apparently due to the difficulty of thoroughly washing out all soluble potassium compounds: for another specimen similarly prepared, but ground up fine in a mortar, gave, after well washing and drying in the air, the following numbers:—

MnO.	K ₂ O.	O.	H ₂ O (by difference).	
79.88	0.37	17.97	1.78	= 100
Oxygen per 100 MnO				= 22.50

Whilst on grinding up in an agate mortar and boiling with water for some time, perceptible amounts of potash salts were dissolved out, and the residue left contained only traces of potash. Hence Görgen's statements as to the non-formation of a manganese dioxide containing potash by heating the nitrate of manganese in presence of potassium nitrate are evidently quite correct, notwithstanding their *à priori* improbability, in view of the decomposition of potassium nitrate and other salts by hydrated manganese dioxide; and, as stated by him, the substance obtained exhibits but little if any deficiency in oxygen.

A notable distinction between this substance and the other bodies examined also was the following: on shaking up with concentrated cold sulphuric acid and allowing to stand for twenty-four hours, the substance subsided leaving a colourless supernatant fluid (manganic sulphate was, however, formed if the liquid were strongly heated). Every other specimen described in this paper gave a pink, violet-pink, or violet supernatant fluid (manganic sulphate, presumably) on treatment with cold acid and clearing by subsidence.

§ 12. Conclusions.

From the preceding experiments, which are partially repetitions of those of Pickering, Kessler, Pattinson, Görgen, Guyard, and others, the following conclusions may be drawn:—

(1.) Manganese dioxide prepared by precipitation processes, and freed from extraneous water is (leaving out of sight metallic oxides carried down with it) a hydrate, $\text{MnO}_2 \cdot \text{H}_2\text{O}$; but it is impossible to keep this hydrate in dry air, as it loses water readily at the ordinary temperature. The rate at which the water is lost appears to be very variable, being the more rapid, *cæteris paribus*, the less combined potash is present; no definite hydrate of any kind, stable in dry air, appears to exist, as every specimen examined continually lost water over sulphuric acid,

even after several months, when the amount of water present was reduced to about 5 per cent.; although one or two specimens were obtained which lost water only slowly when they attained a composition approximating to $3\text{MnO}_2 \cdot 2\text{H}_2\text{O}$, the great majority lost much more water before the rate of further loss became small.

(2.) Neither at the ordinary temperature, at 100° , nor at 210° , does the hydrated substance become anhydrous, even after the lapse of many months in the first case, and hours in the two subsequent cases; the amount of water thus quasi-permanently retained is very variable.

(3.) Neither at the ordinary temperature, nor at 100° , is the expulsion of water accompanied by any material loss of oxygen if indeed any at all is lost: at 210° , however, a slow regular loss of oxygen takes place on continued heating (the substance prepared by heating the nitrate does not lose oxygen thus).

(4.) Hydrated manganese dioxide, if prepared in presence of potassium salts, invariably carries down with it in combination more or less potash: the amount thus fixed varies with the circumstances; in presence of much free acid (nitric, hydrochloric) the amount is lessened, whilst on boiling with caustic potash or digesting at 100° , it appears to become a maximum corresponding nearly with the ratio described by Görgen, viz., $5\text{MnO}_2 \cdot \text{K}_2\text{O}$. In presence of certain potassium salts, *e.g.*, acetate, nitrate, &c., the precipitate appears to decompose a portion of the salt, setting free the associated acid to a greater or a less extent.

(5.) When the precipitation takes place under such conditions that not much potash (or other equivalent metallic oxide) can be carried down by the manganese dioxide, a greater or less deficiency in oxygen (compared with MnO_2) is noticeable in the precipitate; *i.e.*, manganese itself is carried down as MnO in the precipitate. This is especially noticeable when the substance is formed by adding potassium permanganate to excess of manganese sulphate, or when the precipitate is produced by the action of a large quantity of nitric acid on potassium permanganate, or by diluting with water a very acid solution of manganese superchloride (Pickering). Heating the solution appears to diminish the deficiency of oxygen in the precipitate (Guyard).

(6.) By operating in particular ways, the deficiency of oxygen in this precipitate may be reduced to very small limits, or *nil*; for example, adding manganese sulphate to excess of potassium permanganate solution, the liquids being not too concentrated, and at a temperature near 100° (Guyard); adding bromine to a hot solution of a manganese salt in presence of potassium acetate and other potassium salts jointly containing a very large quantity of potassium relatively to the manganese present, or in presence of an acetate and a zinc salt

(Kessler), or of ferric chloride and calcium carbonate (Pattinson), or of zinc carbonate.

(7.) Acting on potassium permanganate solution with reducing agents, such as sulphur dioxide, alcohol, or glycerin, gives rise to a precipitate containing much less available oxygen than corresponds to the manganese present; potash is carried down in combination with the precipitate, but the composition of the latter is very variable. In no case has any substance been obtained of the composition (after drying at 100°) $\text{Mn}_4\text{KH}_3\text{O}_{10}$ (or $8\text{MnO}_2 \cdot \text{K}_2\text{O} \cdot 3\text{H}_2\text{O}$), said by Morawski and Stingl to be always produced under such circumstances; nor is this substance formed by heating precipitated manganese dioxide (containing a little potash) with caustic potash solution for some hours, as stated by them; the product thus obtained approximated to the composition ascribed years ago by Görgeu, viz., $5\text{MnO}_2 \cdot \text{K}_2\text{O}$ (reckoned on the anhydrous substance).

(8.) The statements of Görgeu as to the formation of sensibly pure MnO_2 by heating manganese nitrate to 160° , and the freedom of the pyrolusite-like product from combined potassium, even though potassium nitrate is present in large quantity, are perfectly correct.

(9.) The statements of Volhard as to the formation of *pure* hydrated manganese dioxide by precipitating manganese sulphate with excess of permanganate in presence of nitric acid in the way described by him, are only partially correct, inasmuch as the product contains several per cents. of combined potash, instead of traces only at most, as stated by him; but the manganese and available oxygen in the product are sensibly in the ratio required for MnO_2 .

(10.) The statements of Morawski and Stingl as to the complete expulsion of combined water in hydrated manganese dioxide containing potash, by direct ignition, are only partially correct; almost the whole is thus expelled, but a little is retained, apparently through the formation of KOH , which can be dissolved out of the ignited product by water.

(11.) Long continued ignition in hydrogen removes all, or nearly all, of the potash present in a hydrated manganese dioxide containing potash, leaving behind sensibly pure MnO of a much brighter green colour than that formed by the similar reduction of manganese dioxide free from potash.

(12.) Manganese monoxide retaining a little potash (prepared by reducing dioxide containing potash in hydrogen, but not completely expelling all the potash present) frequently oxidises spontaneously in the ordinary moist air, whereas when free from potash the monoxide does not appear so to oxidise.

(13.) Manganese chloride is sensibly volatile in a stream of HCl gas at a red heat.

(14.) Several different processes for estimating manganese volumetrically have been compared, and the work of Pattinson and Kessler confirmed; sundry new modifications or combinations of previously known processes have been examined, and found to give satisfactory results, the one suggested as most convenient and exact being precipitation by addition *in the cold* of the manganese solution to be determined to excess of permanganate solution containing zinc sulphate, collection on a glass wool filter, and titration with acid ferrous sulphate and permanganate or dichromate solution, preferably standardised in the same way with a manganese solution of known strength.

V.—*The Comparative Value of Different Methods of Fractional Distillation.*

By FREDERICK D. BROWN, B.Sc.

WHERE fractional distillation is carried out on a large scale, various forms of apparatus of a somewhat complicated character are generally employed; though differing much in detail they are all designed to subject the mixed vapours to one or both of two well defined processes, which for the purposes of this paper may be termed respectively *washing* and *cooling*.

In the process of *washing*, the mixed vapours issuing from the still are made to pass through several layers of liquid obtained by their own partial condensation, they are thus *washed* by these successive layers, and it is supposed that the vapour of the liquid of highest boiling point is partially removed by this process, which results therefore in a distillate containing more of the liquid of lower boiling point than would be obtained by simple distillation.

There is at first sight, however, no reason to suppose that a mixture of vapours should be materially altered in composition by a liquid having about the same composition and the same temperature as itself. It would appear that the first step in the construction of these forms of apparatus resulted from an attempt to utilise the latent heat of the vapour given off by a weak spirit to distil a stronger one; the latent heat of the vapour of this second spirit might then be used to distil a third, and so on, thus effecting a series of distillations in the same apparatus with the same fuel. If this series of distillations actually took place, that is to say, if the vapours rising from the still really

condensed in the first layer of liquid, thus causing that liquid to boil and emit vapour, which condensed in the second layer, causing that to boil in its turn, the advantages of the process would be undeniable; but since apparently the vapours only pass through the layers of liquid, and may therefore remain nearly unaltered, the real value of this method of distillation can only be determined experimentally.

In the process of *cooling*, the mixed vapours are partially condensed, either by allowing radiation to take place, or by passing them through a coil kept at a given temperature; the liquid of highest boiling point suffers, of course, the most condensation, and runs back into the still, a better distillate being thus obtained. Now a possible explanation of the success of the first process is that the successive layers of liquid, by obstructing the passage of the vapour, give it more time to cool by radiation, and that thus the two processes are really one and the same.

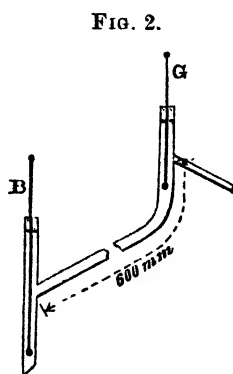
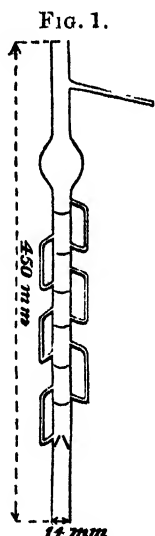
With a view to learning whether these two processes of *washing* and *cooling* really differ in their effects, I have made the experiments now to be described.

Two distillations were first made, one with a form of apparatus advocated by Linneman (*Annalen*, **160**, 195), Le Bel and Henninger (*Compt. rend.*, **79**, 480), and others, designed to wash the vapours, and termed a dephlegmator, the other merely with a long ascending tube, suitable for partially condensing them. The liquids employed were carbon disulphide and benzene, selected for reasons given in a former paper (this Journal, 1879, 547). The composition of the several fractions of the distillates was determined by observing their densities in the manner described in the same paper. All the percentages given below represent the number of molecules of CS_2 in a hundred molecules of the mixture, assuming, of course, that the weights of the molecules of CS_2 and C_6H_6 are to one another as 76 is to 78.

Distillation with Dephlegmator.—547.5 grams of a mixture having a density of 1.07672 at 19.80° , and containing therefore 62.54 per cent. of CS_2 , were distilled from a flask, having a capacity of about a litre, and fitted with a dephlegmator having the form and dimensions shown in Fig. 1; the distillate was collected in the receiver described in the before-mentioned paper (this receiver was used also in all the subsequent distillations). The barometric pressure during the distillation was 773.7 mm. (corrected and reduced to 0°). The following table gives the details of the distillation:—

Number of fraction.	Temperature of distillation.	Weight of fraction.	Density at 19·80°.	Percentage of CS ₂ .
I.....	51·5—52·5	52·34	1·19562	87·71
II.....	52·5—54·0	105·41	1·17857	84·51
III.....	54·0—55·0	63·18	1·16230	81·29
IV.....	55·0—56·5	81·15	1·14912	78·62
V.....	56·5—60·0	28·37	1·11878	72·18
VI.....	60·0—63·0	51·70	1·09150	66·04
VII.....	63·0—70·0	38·31	1·02430	49·00
VIII.....	70·0—75·0	22·44	0·97528	34·39
IX.....	75·0—78·5	27·68	0·91677	14·30
X.....	78·5—80·0	30·69	0·88733	2·84
XI.....	80·0—80·1	31·05	0·88072	0·15

Distillation with Long Tube.—The tube used in this experiment was that shown in Fig. 2. Two thermometers were placed in this tube, one (B) at the bottom, the other (G) at the top; it was thus possible to observe any change which might take place in the temperature of



the mixed vapours as they passed up the tube. 499·3 grams of a mixture having a density of 1·07660 at 19·80°, and containing therefore 62·51 per cent. of CS₂, were distilled; the barometric pressure during the distillation was 771·3 mm. The results are given in the following table:—

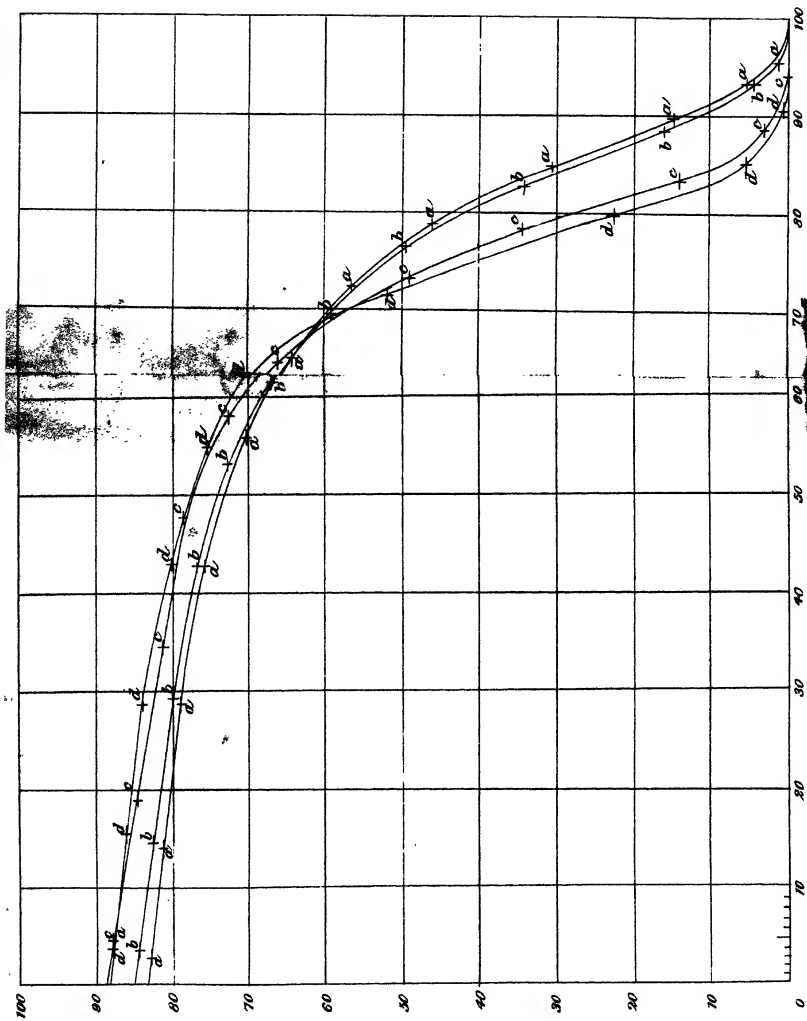
Number of fraction.	Temperature of distillation.		Weight of fraction.	Density at 19°80'	Percentage of CS ₂ .
	B.	G.			
I.....	53°7—54°5	50°5 —51°5	41·00	1·19528	87·65
II.....	54°5—55°5	51°5 —52°25	65·94	1·19047	86·07
III.....	55°5—57°3	52°25—53°5	73·56	1·17604	84·01
IV.....	57°3—60°0	53°5 —55°5	66·69	1·15631	80·11
V.....	60°0—63°5	55°5 —58°0	51·77	1·13432	75·54
VI.....	63°5—67°0	58°0 —61°0	31·46	1·10869	69·97
VII.....	67°0—75°5	61°0 —71°5	51·81	1·03583	52·14
VIII.....	75°5—79°5	71°5 —77°5	31·00	0·94180	23·27
IX.....	79°5—80°6	77°5 —79°7	25·10	0·89356	5·36
X.....	80°6—81°0	79°7 —80°0	28·82	0·88158	0·50

In order to compare the results of these two distillations they must be reduced to some common form; for although the original mixtures contained the same amount of CS₂ in both cases, the weights of the corresponding fractions were not equivalent. The distillations were therefore expressed graphically (see diagram) in the following simple manner:—

Let W = the total weight distilled, $w_1, w_2, w_3 \dots$ = the weights of the several fractions; then $\frac{100 w_1}{W}, \frac{100 w_2}{W}$ &c., will represent the weights of the fractions expressed in hundredths of the total weight W . Now let $y_1, y_2, y_3 \dots$ = the percentages of CS₂ in the several fractions; during the distillation of a fraction the vapour passing over varies in composition, its mean value being represented by the composition of the whole fraction = y . If we suppose that the vapour has this mean composition when exactly half the fraction has passed over, then when the accumulated distillate equals $\frac{50 w_1}{W} = x_1$ the vapour passing over will contain y_1 per cent. of CS₂; when the distillate equals $\frac{100 w_1}{W} + \frac{50 w_2}{W} = x_2$, the vapour passing over will contain y_2 per cent. of CS₂; when it equals $\frac{100 (w_1 + w_2)}{W} + \frac{50 w_3}{W} = x_3$, the vapour will contain y_3 per cent. of CS₂, and so on.

We have therefore the necessary data for determining the points of a curve expressing the variation in composition of the vapour as the distillate passes over, or in other words, the curve gives us the composition of each hundredth of the distillate.

I have included in the diagram the curves representing the two first distillations recorded in the paper previously referred to (this



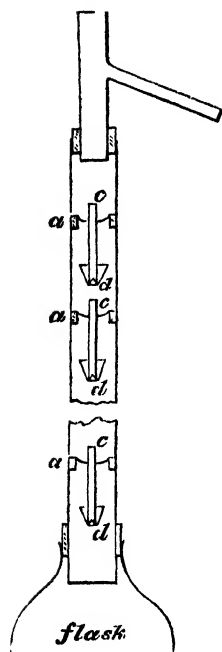
Journal, 1879, Trans., 547), which were made with mixtures containing practically the same amounts of CS_2 , viz., 61.95 per cent. and 61.76 per cent. The following table gives the values of $x_1, y_1; x_2, y_2$, &c., for each of the four distillations, *a* representing the distillation from the retort, *b* that from the flask with **T**-piece, *c* that with dephlegmator, *d* that with long cooling tube:—

<i>a.</i>		<i>b.</i>		<i>c.</i>		<i>d.</i>	
<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>	<i>x.</i>	<i>y.</i>
2.9	82.9	3.6	81.3	4.8	87.7	4.1	87.7
14.3	81.2	14.7	82.5	19.2	81.5	14.8	86.1
28.9	78.8	29.7	79.8	34.6	81.3	28.8	84.0
43.0	75.4	42.9	76.2	47.8	78.6	42.8	80.1
55.9	70.3	53.1	72.5	57.8	72.2	54.7	75.5
65.4	64.1	62.0	66.7	65.1	66.0	63.0	70.0
72.8	56.4	69.9	59.1	73.3	49.0	71.4	52.1
78.9	45.8	76.6	49.5	78.8	39.4	79.7	23.3
84.9	30.6	83.0	33.9	83.4	14.3	85.3	5.4
89.7	15.1	88.7	16.3	88.8	2.8	90.7	0.5
93.9	5.3	93.7	4.5	94.5	0.2	—	—
95.8	0.9	98.1	0.5	—	—	—	—

On examining the four curves obtained by joining each series of points, of which the above numbers are the co-ordinates, we see, firstly, that the **T**-piece, although generally employed merely to immerse the stem of the thermometer in the vapour, was not without considerable influence on the distillation; secondly, that both the dephlegmator and the cooling tube produced much better results than the retort and the flask with **T**-piece; thirdly, that the distillation with the cooling tube was rather better than that with the dephlegmator.

Of these results the last alone calls for further examination. Strictly speaking, the comparison of the distillations *c* and *d* shows that under certain conditions better results can be obtained with a long tube than can be obtained under certain other conditions with a dephlegmator. Those who have had experience with these forms of apparatus will have observed that the rapidity with which the process of distillation is conducted largely influences the result; the amount of cooling surface also cannot be a matter of indifference. In order therefore to compare accurately the two methods, and to see whether the dephlegmator has any special value, the several distillations should be effected in the same time and with the same extent of cooling surface.

FIG. 3.



With this object in view I constructed the dephlegmator represented in Fig. 3; it consists of a glass tube 500 mm. long, and having an internal diameter of 20 mm. This tube carries nine small discs of wire gauze (40 holes to the inch), a piece of brass tube, *cd*, 2.5 mm. in bore and 45 mm. long is passed through the centre of each disc and soldered to the gauze, so that about 8 mm. of the tube project above it. The lower end of each piece of tube is deeply notched with a triangular file, and soldered into a small brass cup *d* (the heads of upholsterer's brass nails serve admirably for these cups). The lower end of the glass tube is fitted with a cork into the flask or still, to the upper end is adapted an ordinary T-piece. The tubes *cd* serve to carry away the liquid from the top of the gauze discs, the cup at the bottom answering as a trap to prevent the vapour passing up the tube instead of going through the gauze. It is essential, when No. 40 gauze is used, that these tubes should be at least 45 mm. long, as the adhesion of the

liquid to the gauze is so considerable that the pressure of the vapour underneath is sufficient to force the liquid out of a shorter tube; with finer gauze a still longer tube must, of course, be employed. In the figure the discs of copper gauze are drawn fitted into small rings of cork; this not only holds them more firmly, but also causes the whole of the condensed liquid to accumulate on their upper surfaces instead of running down the side of the glass tube; the cork would, of course, be unsuitable for liquids of high boiling point.

This dephlegmator was constructed only with a view to the ready removal of the discs, &c., so that the same tube might be used with and without them. The simple construction, the absence of fragility, and the fact that under no circumstances does it get overloaded with condensed liquid, are, however, advantages which render it preferable to those ordinarily used.

I now attempted to carry out two distillations with the same liquid in the same length of time, one with the gauze discs, the other without. I found, however, that this could not be done even when a gauge was fitted to the Bunsen burner used, and the gas maintained at a constant pressure by means of a screw clamp. Three distillations were therefore made with the discs and two without; these, as will be seen, were sufficient to show whether the two methods were identical

or not. In each case 1000 c.c. of a mixture of benzene and carbon disulphide containing about 62·7 per cent. of CS_2 was employed. The density of the benzene at $19\cdot80^\circ$ was 0·88049, that of the carbon disulphide was 1·26629; they were both carefully purified, and their densities were so nearly the same as those of the liquids previously used, viz., 0·88034 and 1·26642 that the same table of densities and percentages was employed. The distillation was continued until four fractions of 200 c.c. each had passed over; it was then stopped, and the densities of the four fractions and of the residue were observed; the results were as follows:—

I. *Distillation with gauze discs. Mixture containing 62·77 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	29	$^\circ - 51\cdot95$	1·19842	88·23
II	30	$51\cdot95 - 54\cdot20$	1·17757	81·31
III	41	$54\cdot20 - 60\cdot0$	1·14811	78·41
IV	97	$60\cdot0 - 80\cdot0$	0·98993	38·78
Res.	—	—	0·88027	00·00

II. *Distillation with gauze discs. Mixture containing 62·70 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	54	$^\circ - 50\cdot2$	1·21959	92·02
II	54	$50\cdot2 - 52\cdot0$	1·20705	89·83
III	52	$52\cdot0 - 67\cdot0$	1·14022	76·77
IV	95	$67\cdot0 - 80\cdot0$	0·94429	24·15
Res.	—	—	0·88019	00·00

III. *Distillation with gauze discs. Mixture containing 62·82 per cent. of CS_2 .*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to $19\cdot80^\circ$.	Percentage of CS_2 .
I	85	$^\circ - 50\cdot1$	1·22877	93·66
II	40	$50\cdot1 - 53\cdot5$	1·18559	85·84
III	60	$53\cdot5 - 62\cdot2$	1·14599	77·97
IV	73	$62\cdot2 - 80\cdot6$	0·92097	15·85
Res.	—	—	0·88054	00·00

IV. *Distillation with same tube without gauze. Mixture containing 62.74 per cent. of CS₂.*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to 19.80°.	Percentage of CS ₂ .
I	45	— — 52.6	1.19066	86.79
II	45	52.6 — 54.9	1.17413	83.63
III	40	54.9 — 60.8	1.13420	75.52
IV	36	60.8 — 77.2	1.01833	47.31
Res.	—	— —	0.88756	2.93

V. *Distillation without gauze discs. Mixture containing 62.54 per cent. of CS₂.*

Number of fraction.	Time occupied in distilling.	Temperature of distillation.	Density corr. to 19.80°.	Percentage of CS ₂ .
I	225	— — 50.7	1.20960	90.30
II	300	50.7 — 54.6	1.20032	88.58
III	285	54.6 — 66.1	1.14887	78.57
IV	225	66.1 — 80.5	0.93691	21.56
Res.	—	— —	0.88053	0.00

On inspecting these numbers we see, in the first place, that they afford convincing proof of the statement previously made that the rate of distillation is an element of considerable importance, showing that the slower the distillation the more carbon disulphide does the distillate contain, and that this is equally the case whether the vapours are washed or not. In comparing together the percentages of the various fractions it must, of course, be remembered that only the first fractions of each distillate are strictly comparable, for after these had passed over, the liquid in the still had no longer the same composition in each successive distillation. This explains, for instance, why the third fraction of the first distillation contained more CS₂ than that of the third, though it distilled in a shorter time. In the first case a less quantity of CS₂ had been previously removed; at the beginning of the third fraction therefore the liquid in the still was much richer in CS₂.

These distillations further prove conclusively that the processes of *washing* and of *cooling* are not identical. The fifth distillation was made under the most advantageous circumstances, that is, it was conducted at the slowest possible rate, yet the result was decidedly inferior to that of the second in which the vapour was washed, and which was completed in a fourth of the time. The same remark applies to the fifth and third, and to the fourth and first distillations. Since in equal times with equal surfaces the radiation must be the same, the effect of radiation in the fifth case must have been greater than in the second; the better result in the second case must there-

fore have been due to the presence of the gauze discs. A certain amount of secondary distillation does therefore take place in the dephlegmator, and the question whether the apparatus has any special value is answered in the affirmative.

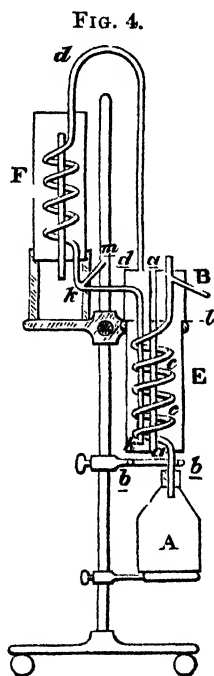
Notwithstanding this result, we are not yet in a position to state that the dephlegmator is the best apparatus for fractional distillation, and that because we have by no means exhausted the resources of the process of *cooling*. The mixed vapours in passing up a tube may obviously be subjected to more and more radiation if the tube be gradually increased in length, until at last no vapour will reach the top of the tube; the best possible result will be obtained when the vapour just creeps over the top, before complete condensation takes place, having then reached its lowest possible temperature. It would of course be impracticable to effect distillations in this way, but the object in view is readily attained by passing the vapours through a tube or still head maintained at a given temperature, as is done every day when distillations are carried out on a manufacturing scale.

If the temperature of the still head be the lowest possible compatible with the passage of vapour into the condenser, the result will be the best which the process admits of.

The next step in this investigation was therefore to make a suitable apparatus for the above purposes, the general character of the one finally adopted is shown in Fig. 4.

The still A communicates with a coil C, terminating in a vertical portion open at the top, into which a thermometer is fitted with a cork in the usual manner; a lateral tube B serves to conduct the vapour from the coil into the condenser. The whole of the coil C, including the junction with the tube B, is enclosed in a cylindrical copper box 300 mm. long by 110 mm. in diameter.

The two ends of this cylinder are tied together by means of the copper tube *aa*, which not only strengthens the cylinder, but, being open at the top, serves for the introduction of a second thermometer, which indicates its temperature. This copper box is filled up to the level *l* with a liquid or mixture of liquids boiling at the required temperature, the heat being furnished by a ring burner, *bb*. The vapour given off by this boiling liquid passes up the tube *dd* to the condenser F, whence it returns in a liquid form by the tube *kk* to the bottom of the box E.



The small tube *m* serves as a communication with the atmosphere. As there is considerable trouble in changing from one liquid to another when a different temperature is required, the apparatus is completely closed except at *m*, by connecting *m* with an air chamber, in which any constant pressure can be conveniently maintained; the boiling point of the liquid in *E* can be altered at will. With a view to the use of the apparatus in this manner, the copper box *E* and the tubes connected with it were tested at a pressure of 100 lb. on the square inch.

In employing this apparatus, the ring burner *bb* is first lighted, when the liquid in *E* begins to boil, the temperature as indicated by the thermometer in *au* (this tube is filled with water or petroleum) soon becomes constant, and at the same time the reading of the thermometer placed in the top of the coil ceases to vary; heat is then applied to the still *A*, and the distillation carried out as rapidly as can be done without altering the reading of the thermometer in the coil.

For the first distillation made with this apparatus, methylated spirit was put in the box *E* and the pressure maintained was such that ebullition took place at about 57°. About 800 grams of a mixture of benzene and carbon disulphide were put in the still *A*, and the distillation collected in 10 fractions.

The mixture in the still at the beginning of the distillation contained 45·00 per cent. of CS_2 ; at the end it contained 26·56 per cent. The barometric pressure during the distillation was 750·7 mm.

The thermometer *B* was placed in *aa*, the thermometer F_2 in the top of the coil. The details of the distillation were as follows:—

No. of fraction.	Reading of <i>B</i> when fraction removed.	Reading of F_2 when fraction removed.	Density of fraction at 19·80°.	Percentage of CS_2 in fraction.
I	57·50	57·10	1·13523	75·73
II	57·50	57·10	1·13185	75·02
III	57·50	57·10	1·13348	75·36
IV	57·50	57·10	1·13528	75·74
V	57·52	57·12	1·13649	75·99
VI	57·51	57·10	1·13656	76·01
VII	57·53	57·12	1·13733	76·17
VIII	57·53	57·30	1·13819	76·35
IX	57·53	58·00	1·13358	75·38
X	57·53	57·90	1·13333	75·33

The slight rise in the reading of F_2 towards the end of the distillation was due to the vapour passing too rapidly through the coil; it did not seem, however, to have any influence on the composition of the distillate.

A second distillation was made with 600 grams of a mixture containing 11.47 per cent. of CS_2 ; the barometric pressure was 753.1 mm. At the end of the experiment the liquid remaining in the still contained only 4.33 per cent. of CS_2 ; the details were as follows:—

No. of fraction.	Reading of B when fraction removed.	Reading of F_2 when fraction removed.	Density of fraction at 19.80° .	Percentage of CS_2 .
I.....	70.29	69.94	.98826	38.14
II.....	70.35	69.98	.98516	37.48
III.....	70.57	70.23	.98498	37.42
IV.....	70.56	70.24	.98527	37.52

These two distillations show that the composition of the distillate is independent of the amount of carbon disulphide in the still, but varies with the temperature of the coil or still head.

Two distillations were now made with the copper cylinder E filled with pure carbon disulphide, the boiling point of this liquid being evidently the lowest temperature at which any vapour given off by a mixture of benzene and carbon disulphide can pass into the condenser. In the first of these distillations a mixture containing 42.69 per cent. of CS_2 was employed, while the residue in the still when the experiment was stopped contained 32.37 per cent. of CS_2 ; the amount of CS_2 in the various fractions of the distillate was found to vary between 97.32 per cent. and 98.72 per cent. The distillate did not gradually increase or diminish in density, the higher and lower percentages following each other indiscriminately. In the second distillation, for which the liquid remaining from the first was used, the liquid in the still contained at the beginning 32.37 per cent., and at the end 25.21 per cent. of CS_2 ; in this case the amount of CS_2 in the distillate varied from 97.48 per cent. to 99.19 per cent.

These two experiments show that when the still head is maintained at a temperature equal to the boiling point of the most volatile compound in a mixture, that compound alone, or nearly alone, passes over into the condenser; it is therefore possible by the use of this apparatus to effect an almost complete separation of the various constituents of a mixture of volatile substances in one distillation.

In order to show the practical value of the method, I may mention that I have frequently used it to separate benzene from the toluene and other substances which ordinary commercial benzene contains in large quantities.

The benzene thus obtained has always been nearly pure. As an example, the following rectification of some crude benzene will suffice. A sample of 200 c.c. of this liquid was distilled in an ordinary flask; it

began to distil at 83° ; at 90° 120 c.c. had accumulated in the receiver, at 95° 153 c.c., at 100° 168 c.c., at 105° 179 c.c., and at 110° 192 c.c. 1100 c.c. of this very impure liquid were distilled with the apparatus above described, maintained at a temperature of 81° ; this was rather too high to give a really good result; nevertheless 500 c.c. of rectified benzene were obtained, of which a sample of 200 c.c. distilled as follows:—Distillation commenced at 80.0° ; at 80.4° 155 c.c., at 80.8° 176 c.c., at 81.0° 180 c.c., and at 82.0° 191 c.c. had accumulated in the receiver. When 500 c.c. of this rectified benzene had passed over the experiment was stopped, and a sample of the residue distilled as follows:—Distillation commenced at 91° ; at 95° 80 c.c., at 100° 130 c.c., at 105° 158 c.c., at 110° 186 c.c. had passed into the receiver; it is therefore seen from how impure a liquid pure benzene may be directly obtained.

As regards the results contained in the above paper, it may be contended that they present but little novelty; it was, however, necessary that the effects obtained by the different methods should be exactly defined and numerically stated before a complete explanation of fractional distillation could be advanced.

VI.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. III.—*On the Influence exerted upon the Course of Certain Chemical Changes by Variations in the Amount of Water of Dilution.*

By M. M. PATTISON MUIR, Caius Prælector in Chemistry, and CHAS. SLATER, B.A., Scholar of St. John's College.

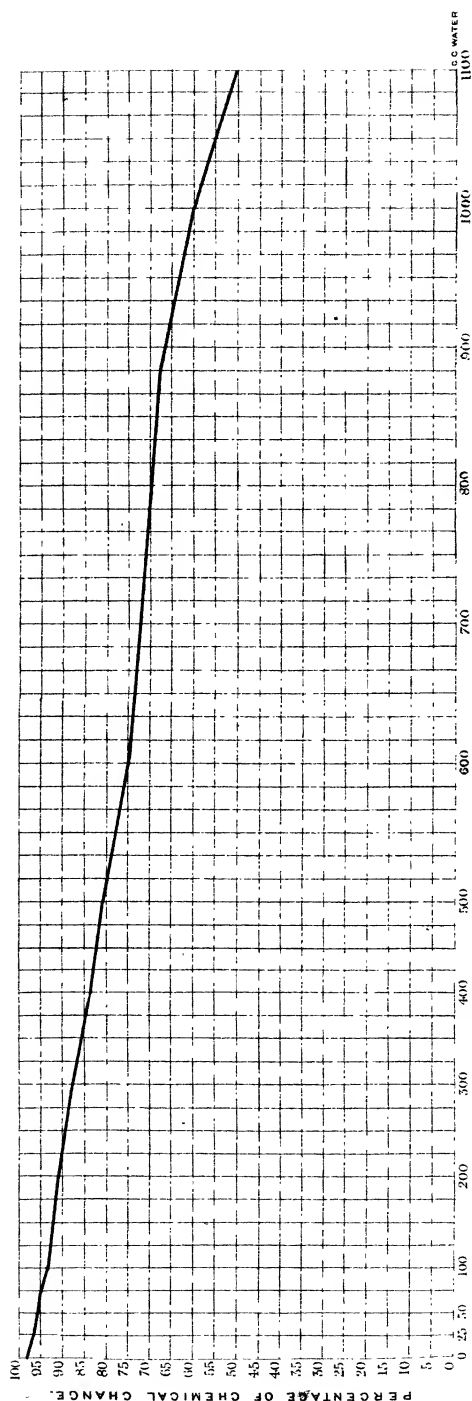
1. In a paper by one of us (this Journal, 1879, Trans., p. 311) an experimental examination was made of some of the conditions which affect the equilibrium of the system $\text{CaCl}_2 + \text{Na}_2\text{CO}_3 + x\text{H}_2\text{O}$. It was there suggested that a study of the changes undergone by this system under conditions such that the action of the various forces might be more disentangled from one another would be advisable.

The present paper contains the results of experiments undertaken with the object of determining the influence on the equilibrium of the system of variations in the quantity of water present.

2. The solutions used contained respectively 320.7 mgrms. CaCl_2 in 10 c.c., and 305.54 mgrms. Na_2CO_3 in 8.1 c.c. The sodium carbonate

PLATE I. (TABLE I.)

CaCl_2 and Na_2CO_3 . 1:1 molecules. 30 minutes. 13°.



was added to the calcium chloride solution, and the whole was then shaken up.

Initial condition was $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 330$ mols.

Each 25 c.c. water added = 470 mols. Time = 30 minutes.
Temp. = 16—18°.

TABLE I.

Water added.		Mean percentage of CaCO_3 produced.	Actual numbers obtained.					
In c.c.	In mols.							
0	330	97·8	97·5		98·2			
25	800	96·3	96·8		96·1	96·03	96·03	
50	1270	96·0	95·1	96·03	96·03	96·08	95·8	95·8
75	1740	95·5	95·7	95·4				
100	2210	93·8	94·6	93·1	94·3	93·3		
200	4090	91·2	91·2	91·2	91·2			
300	5970	86·3	85·9	85·9	87·1			
400	7850	85·8	85·8	85·8	85·6			
500	9730	82·1	78·7	78·7	85·3			

Another solution was used after this point. 10 c.c. CaCl_2 = 55·5 mgrms.

Initial state = 1 : 1 : 2700 mols. Each 25 c.c. water added = 2700 mols.

Water added.		Mean percentage of CaCO_3 produced.	Actual numbers obtained.	
In c.c.	In mols.			
100	12,500	75·0	75·0	
175	20,600	66·5	66·0	67·0
200	23,300	62·2	62·2	
225	26,000	52·0	52·0	

The results contained in this table are graphically represented in the curve of Plate I.

3. These results show that in the special case considered the amount of chemical change decreases regularly as the amount of water of dilution increases. The water which is added appears to exert a purely mechanical influence on the change under consideration.

We may suppose that the chances of collision between the molecules of sodium carbonate and calcium chloride are decreased the greater the number of inactive water molecules interposed.

4. In the second series of experiments which we conducted the influence of water on the reaction $\text{SrCl}_2 + \text{H}_2\text{SO}_4 = \text{SrSO}_4 + 2\text{HCl}$ was studied. The results obtained were very discrepant, and seemed to allow of no reasonable generalisation being deduced. These results will be referred to in the sequel.

5. The reaction $\text{BaCl}_2 + \text{K}_2\text{C}_2\text{O}_4 = \text{BaC}_2\text{O}_4 + 2\text{KCl}$ appeared to

present a chemical change well adapted for the study of the influence of dilution.

Barium oxalate is tolerably insoluble in water, and the amount of change can be quickly and accurately determined by measuring the quantity of undecomposed potassium oxalate by titration with standardised permanganate.

The experiments were conducted by adding a measured volume of potassium oxalate solution to the proper quantity of solution of barium chloride previously diluted with a measured volume of water, shaking up, and then allowing to remain at rest. At the close of the time allowed for the change to proceed, a portion of the clear liquid was drawn off and run through a dry filter into a dry beaker, and the amount of potassium oxalate in solution was determined in an aliquot portion of this filtrate.

TABLE II.

10 c.c. BaCl_2 solution used = 627.04 mgrms. BaCl_2 : 9.35 c.c. $\text{K}_2\text{C}_2\text{O}_4$ solution used = 501.03 mgrms.

Initial condition = BaCl_2 : $\text{K}_2\text{C}_2\text{O}_4$: H_2O = 1 : 1 : 360 mols.

Each 25 c.c. water added = 460 mols. Time = 30 mins. Temp. = 16–18°.

Water added.		Mean percentage of BaCl_2 decom- posed.	Numbers actually obtained.			
In c.c.	In mols.					
0	360	90.2	89.09	91.32		
25	820	88.5	88.2	88.8		
50	1,280	87.6	87.5	87.8		
100	2,200	79.8	79.1	80.2	79.3	79.9
200	4,040	74.8	75.0	74.5		
250	4,960	70.3	70.4	70.1		
300	5,880	69.1	70.0	67.8	69.5	
350	6,800	63.2	62.8	63.5		
400	7,720	56.8	57.5	57.5	55.4	
600	11,400	46.0	43.0	49.0		

These results are represented graphically in Curve A, Plate II.

6. The generalisation of par. 3 may, we think, be also deduced from these results. The amount of chemical change decreases regularly as the amount of water of dilution increases.

7. Another series of experiments was conducted similar to the foregoing, save that the beakers in which the change proceeded were surrounded by ice.

TABLE III.

Details as before. Temp. = 3°. Time = 30 mins.

Water added. In c.c.	Mean percentage of In mols. BaCl ₂ decomposed.	Numbers actually obtained.						
0	360	83.7	85.5	82.0				
25	820	81.6	81.5	81.8				
100	2,200	74.8	76.1	77.5	73.1	72.5		
200	4,040	69.6	68.7	69.0	71.0			
300	5,880	61.2	60.5	61.9				
400	7,720	45.8	49.5	43.7	44.1	49.4	44.1	49.4
600	11,400	12.3	12.3					
700	13,240	9.3	9.3					

These results are represented graphically in Curve B, Plate II.

8. In the next series of experiments we made the time longer, still keeping the temperature low.

TABLE IV.

Details as before. Temp. = 3°. Time = 90 mins.

Water added. In c.c.	Mean percentage of BaCl ₂ In mols. decomposed.	Numbers actually obtained.			
25	820	98.1	98.1		
50	1,280	97.5	97.5		
100	2,200	92.0	92.1	91.9	
200	4,040	83.9	83.9	83.8	
300	5,880	71.5	70.7	69.9	73.0
400	7,720	63.7	63.8	65.8	61.5
500	9,560	44.6	46.4	42.8	
600	11,400	30.7	25.8	32.5	33.8
700	13,240	20.1	23.9	16.3	
800	15,080	24.4		24.4	24.4 24.4

These results are represented graphically in Curve C, Plate II.

9. We now raised the temperature, keeping the time the same as before.

TABLE V.

Details as before. Temp. = 18°. Time = 90 mins.

Water added.		Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.			
In c.c.	In mols.					
25	820	98.2	98.2			
50	1,280	96.3	96.8	96.3		
100	2,200	94.0	95.5	92.5		
200	4,040	88.2	91.2	85.2		
300	5,880	80.5	81.4	79.7		
400	7,720	67.0	68.9	65.1		
500	9,560	49.9	47.4	52.4		
600	11,400	32.5	34.2	32.2	33.7	31.8
700	13,240	24.8	—	24.8		
800	15,080	10.3	10.3	10.8	9.7	

These results are graphically represented in Curve D, Plate II.

10. Curve B (Plate II) seems to us to show that with a low temperature and a short time (30 minutes), the process of chemical change is retarded to a proportionately greater extent by a large, than by a small quantity of water of dilution. Curve C, which exhibits the influence of the water of dilution at a low temperature, but when the change is allowed to proceed for a longer time (90 minutes) shows the same irregularity in the action of the diluting water. And from Curve D we conclude that when the change is allowed to proceed for a considerable time (90 minutes), the retarding influence exerted by large masses of diluting water is proportionately greater than that exerted by small masses, even when the temperature is allowed to rise to 16° or 18°.

11. In order to explain these results we advance the hypothesis that under the conditions of experiment a number of hydrates of barium chloride tend to form in the solution. Among these hydrates we regard the cryohydrate as occupying an important place.

At moderate temperatures (18°) and short times (30 minutes) we suppose that the tendency to formation of cryohydrate is very small; hence the regular action of the water of dilution (Curve A). At low temperatures, however, even if the time be short, the cryohydrate (along with other hydrates, doubtless) tends to form, and being produced in presence of a large mass of one of the products of its own dissociation, this cryohydrate is somewhat stable. The greater the mass of water, the greater the stability of the cryohydrate, other conditions being constant and any secondary action which may be exerted by the water being disregarded.

When we make the time of action longer, the tendency to formation

PLATE II. (TABLES II to V.)
 BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$, 1:1 molecules.
"Titration Curves."

Journ. Chem. Soc. Feb. 1880.

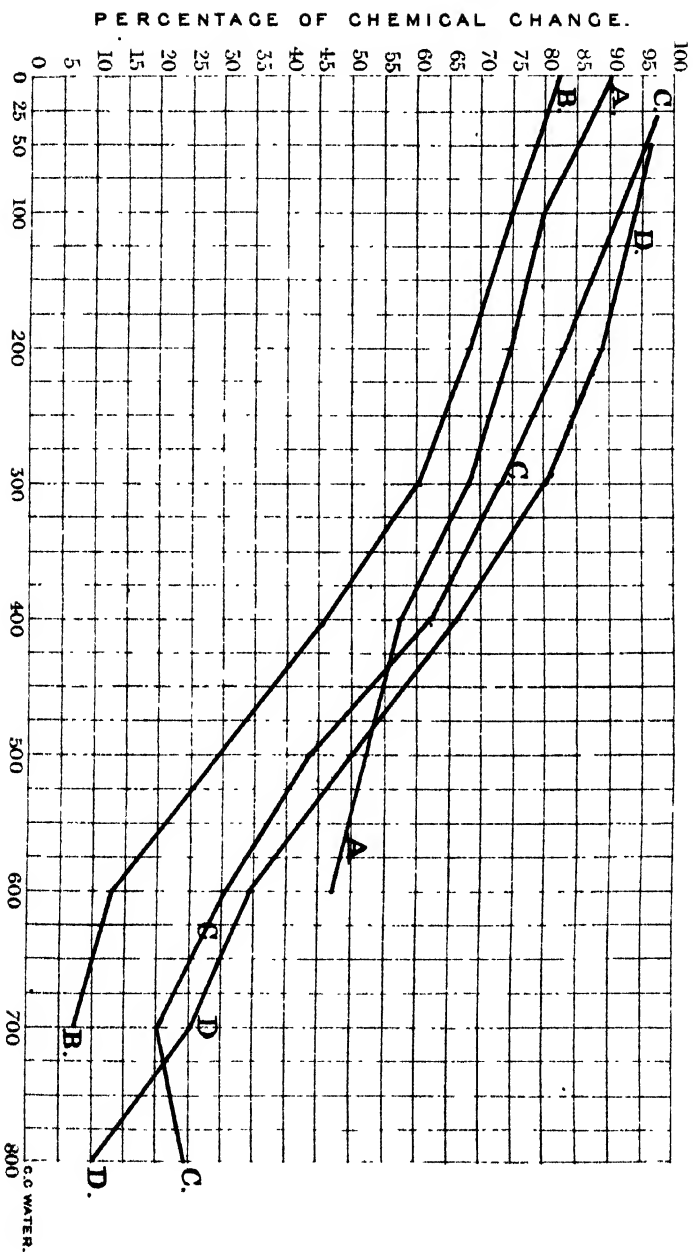
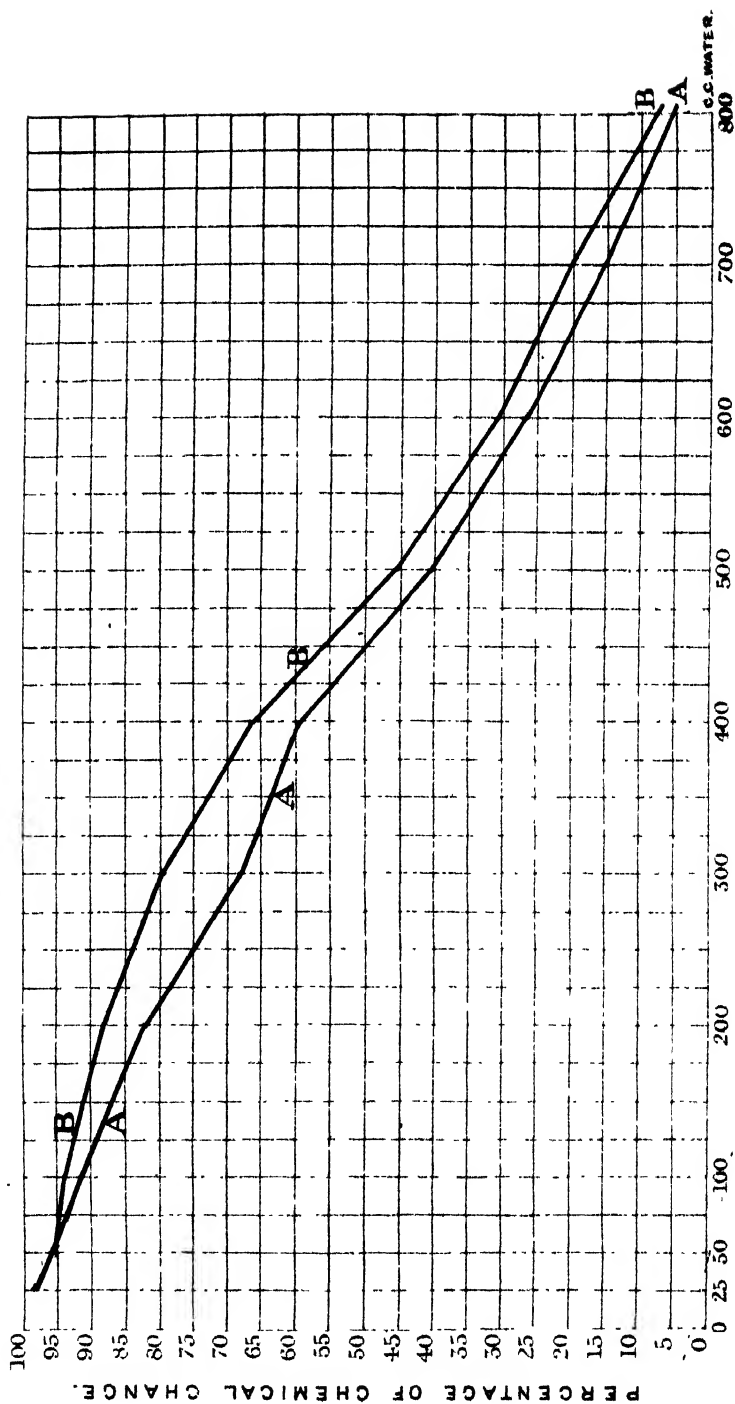


PLATE III. (TABLES VI and VII)

BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$. 1:1 molecules.

"Pipetting Curves"



of cryohydrate might be expected to become greater, and therefore the Curve C might be expected to approach to or even to overlap the Curve B. But long time of action increases the chance of molecular collisions, and hence of molecular decompositions. Curve C keeps always above Curve B, but exhibits the same general form.

But that time does tend to production of cryohydrate (by our hypothesis), even when temperature rather tends to dissociation of the same, provided the presence of a large quantity of the liquid product of such dissociation be insured, is shown by Curve D, which exhibits much the same general form as B and C.

Now the association of water molecules to the molecules of barium chloride must be attended with loss of energy from the entire system, hence the amount of chemical change becomes proportionately less as the velocity of formation of these complex molecules (by hypothesis) increases.

12. In the next series of experiments the condition of time was arranged so that the precipitated barium oxalate should have completely settled down, leaving a clear supernatant liquid, before the close of the action. A portion of the clear liquid was drawn off by means of a pipette and aspirating arrangement, and the quantity of undecomposed oxalate was determined therein without previous filtration.

TABLE VI.—*Pipetting.*

Details as before. Time = 90 mins. Temp. = 3°.

Water added.		Mean percentage of BaCl ₂ decom- posed.	Numbers actually obtained.				
In c.c.	In mols.						
25	820	98.1	98.1				
50	1,280	97.5	97.5	97.5			
100	2,200	91.6	92.1	91.1			
200	4,040	82.0	81.6	82.5			
300	5,880	67.8	68.4	67.2			
400	7,720	58.0	58.3	57.8			
500	9,560	41.8	42.8	40.8			
600	11,400	27.6	26.2	29.0			
700	13,240	15.0	12.9	16.6	10.2	18.1	17.2
800	15,080	5.0	4.5	5.5			

Curve A, Plate III, represents these results in graphic form.

13. A series of experiments similar to those just detailed was carried out at a higher temperature.

TABLE VII.—*Pipetting.*

Details as before. Time = 90 mins. Temp. = 16—18°.

Water added.		Mean percentage of BaCl ₂ decom- posed.	Numbers actually obtained.			
In c.c.	In mols.					
25	820	98.2	98.2	—	—	—
50	1,280	96.4	96.3	96.8	96.0	—
100	2,200	93.5	94.5	92.5	—	—
200	4,040	88.4	90.9	85.9	—	—
300	5,880	80.0	80.0	80.0	—	—
400	7,720	65.9	68.2	63.7	—	—
500	9,560	44.3	42.8	45.8	—	—
600	11,400	31.2	31.4	31.8	30.6	31.0
700	13,240	20.6	18.6	18.9	24.4	—
800	15,080	4.5	4.0	4.0	5.5	—

See Curve B, Plate III.

14. These results are, we think, in keeping with the hypothesis of par. 11.

Curve A shows, it is true, an almost regular retarding influence exerted by the water of dilution, but we believe that the "pipetting method" of estimation is more delicate than the "filtration method," and that the influence of formation of cryohydrate, &c., is shown by the former method in the early as well as in the later portions of the curve.

Curve B, where the temperature is higher, and, therefore, where one of the conditions of formation of cryohydrate is not fulfilled, exhibits the special influence of water of dilution under consideration only when the quantity of water becomes somewhat large. The same general deduction may be made from the analogous filtration Curve D, Plate II.

15. In repeating some determinations in succeeding portions of the same liquid filtered from barium oxalate, we were astonished to find great discrepancies between the results. If 50 c.c. were withdrawn from the filtrate immediately that, or approximately that quantity of liquid had passed through the filter, the quantity of undecomposed oxalate therein was found to be considerably greater than the quantity contained in the succeeding 50 c.c. withdrawn from the filtrate, filtration being continued with little or no intermission.

We, therefore, made a series of determinations of the influence of water of dilution on the change under consideration, the data being obtained from estimation of undecomposed oxalate contained in the second 50 c.c. of liquid which passed through the filter.

PLATE IV. (TABLE VIII)

BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$ 1:1 molecules.

Comparison of "Pipetting" and "Filtration Curves" at 3°.

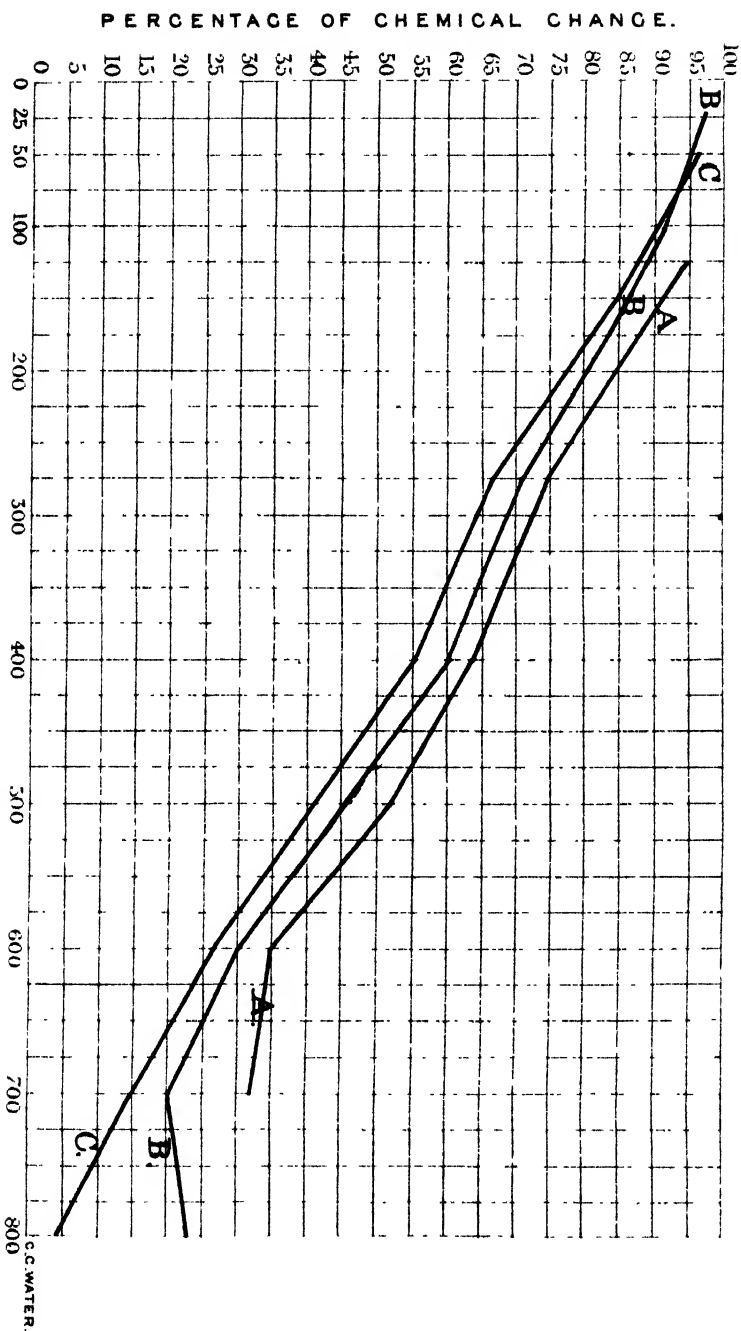


PLATE V. (TABLE VIII).
BaCl₂ and K₂CO₃. 1:1 molecules.

Journ. Chem. Soc. Feb. 1889.

Comparison of "Pipetting" and "Filtration Curves" at 18°

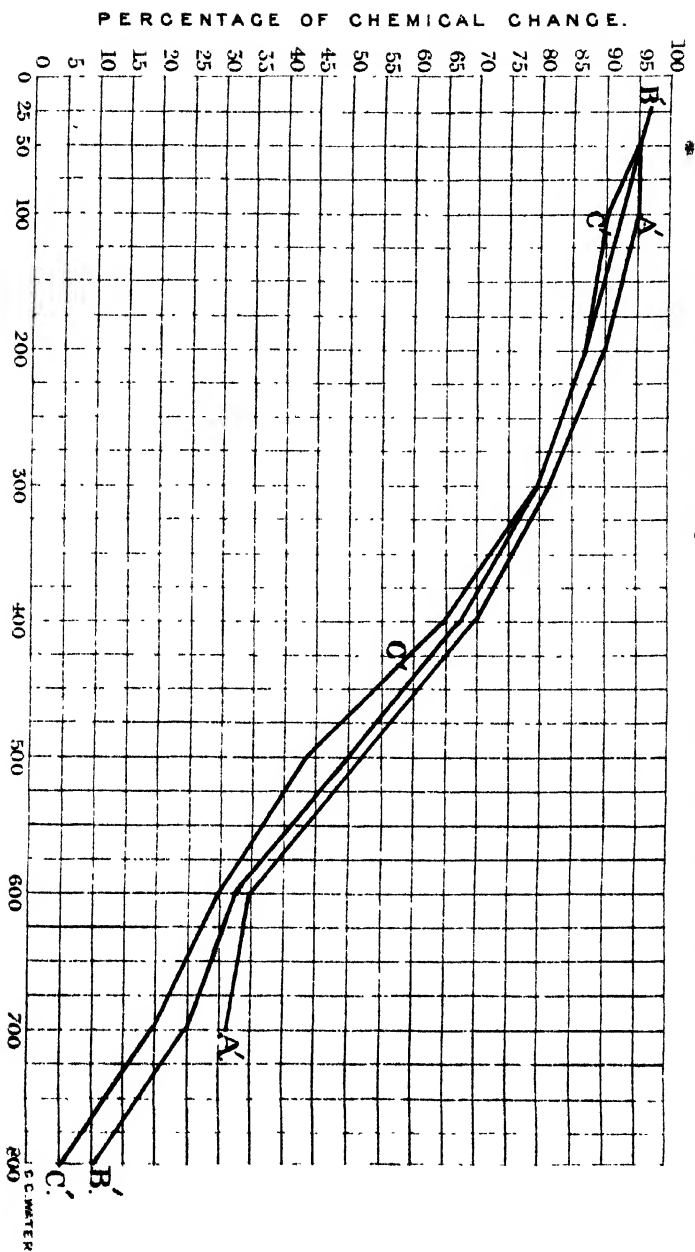


TABLE VIII.—*Second Filtrates.*

Series A. Details as before. Time = 90 mins. Temp. = 3°.

In c.c.	Water added.		Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.			
	In mols.						
100	2,200		93.4	93.7	93.1		
300	5,880		71.6	70.0	73.2		
500	9,560		52.6	50.8	54.4		
600	11,400		34.9	32.5	37.3		
700	13,240		34.2	32.5	36.0		

Series B. Time = 90 mins. Temp. = 18°.

100	2,200	95.4	96.0	94.8			
200	4,040	89.0	91.5	86.5			
300	5,880	80.8	81.9	79.7			
400	7,720	67.4	69.9	65.0			
500	9,560	51.1	53.8	48.4			
600	11,400	35.3	36.0	34.7			
700	13,240	32.5	35.7	32.3	31.0	30.4	

In Plates IV and V these results are graphically represented by Curves A and A' respectively. The Curves B and C of Plate IV, and B' and C' of Plate V, represent the results of "pipetting" and "first filtrate" determinations under the same conditions of time and temperature as those under which the data of A and A' were determined.

16. From the curves of Plate IV it is apparent that the influence exerted by water of dilution on the chemical change under consideration, at low temperatures and moderate degrees of dilution, is much the same whether the data be obtained by analyses of the liquids removed from above the precipitated barium oxalate, by pipetting, or by filtration. When, however, large amounts of water are added, the results show considerable differences, according as the pipetting or filtration process is adopted, the latter process exhibiting the change as proceeding to a greater extent than the former.

We think that these results may be explained by supposing that at a low temperature and with much water the tendency to formation of cryohydrate reaches a maximum, and that under these conditions the whole system of chemical molecules is thrown into a state of strain from which it is partly relieved by the process of filtration, the result of this relief being that the molecular equilibrium is upset, and that the velocity of the decomposition of barium chloride by potassium oxalate is suddenly increased.

If there be elements of truth in this explanation, we should expect to find smaller differences in the results obtained by the methods—

pipetting and filtration—when the conditions of experiment were rendered less favourable to formation of cryohydrate molecules. One less favourable condition is maintenance of higher temperature. The curves of Plate V (when compared with those of Plate IV) show that the results obtained from “pipetted liquid,” “first filtrate,” and “second filtrate” respectively, agree much more closely when the temperature is 18° than when the temperature is 3° .

Again, with small quantities of water of dilution, *i.e.*, with a condition unfavourable to formation of cryohydrate, the differences between the results obtained by the “pipetting,” and those by the “first filtrate” methods are reduced almost to zero, even at 3° ; at this temperature “pipetted” results differ slightly, but only slightly, from “second filtrate” results, while at 18° the results obtained by both methods are almost identical. A small number of experiments carried out at a higher temperature, 50° , showed that identical results are obtained at this temperature by the three methods with a dilution of 400 c.c. and 800 c.c.

It is difficult to foretell what influence would be exerted on the general stability of the system at a low temperature by variations in the time of action. The numbers obtained by us seem to show that the system is in a state of greater strain at 3° , after the expiry of 30 minutes than when 90 minutes have elapsed. Thus the mean percentages of barium chloride decomposed at 3° after 30 minutes' action, as measured by analysis of the first and second 50 c.c. of filtrate, were respectively:—

c.c. water added.	First 50 c.c.	Second 50 c.c.	Difference.
100	74·8	77·3	2·5
300	61·2	71·4	10·2
400	45·8	68·4	22·6

The results obtained under the same conditions, save making time = 90 minutes, are stated for sake of comparison.

c.c. water.	First 50 c.c.	Second 50 c.c.	Difference.
100	92·0	93·4	1·4
300	71·5	71·6	0·1
400	63·7	65·0	1·3

The system would thus appear to be in a state of maximum strain when the conditions favourable for formation of cryohydrate are ensured, *viz.*, low temperature and much water, and when the time of action is short. We are almost inclined to believe that under these conditions the cryohydrate molecules are in process of formation, whilst after a longer time the molecules are, to a great extent, formed,

and that therefore the system, although yet very unstable, is nevertheless more stable than it was under the former time conditions.

17. We do not attempt to propound any exact hypothesis as to the action of the filter in inducing a sudden increase in the velocity of the chemical change. It may be that the reacting molecules are brought into closer contact in the pores of the filter,* or it may be that when a portion of the liquid, the constituents of which are by our hypothesis in a state of strain, is removed from the main liquid, decomposition is induced in the separated portion by the small change of temperature which is undergone by the solution during its passage through the filter, or perhaps by the mechanical action of the surface of paper to which the solution is for a time exposed.

A few determinations were made of the amount of change when calculated from data obtained by analyses of the third 50 c.c. of filtrate. These determinations were almost identical with those obtained from the second 50 c.c., but considerably higher than those obtained from the first 50 c.c. of filtrate.

The results obtained by the pipetting and filtration methods are stated in percentages of total barium chloride decomposed: the rapid change which occurs while filtering under certain conditions of dilution and temperature, occurs in that small isolated portion of the general chemical system which is placed upon the filter, but the amount of change is calculated as if that change proceeded to the same extent within the whole liquid. The exposure of the whole liquid to a very slightly higher temperature, or to passage through a filter, would not necessarily produce a change to the same extent as is produced in the small isolated portion.

Certain experiments, which we have not as yet continued, seemed to show that, if, when strontium sulphate is precipitated from a dilute solution of the chloride by addition of sulphuric acid, and when the liquid above the precipitate is perfectly clear, a portion of this clear liquid be isolated from the main portion by withdrawal in a pipette, the clear liquid so isolated quickly becomes turbid, because of renewed precipitation of strontium sulphate.

18. The individual results contained in many of the foregoing tables show considerable discrepancies among themselves; these discrepancies are not, however, in our opinion, contradictory of the hypothesis which we have advanced.

The method of determining the amount of chemical change which we have used is fitted to give fairly accurate results if the mean of several determinations be adopted, but the occurrence of small differences between the numbers actually obtained is to be expected.

The discrepancies are most marked when dealing with dilute solu-

* In connection with this, compare Bayley, this Journal, 1878, Trans., p. 304.

tions, a low temperature and a short time of action; they become less marked when the temperature is high, the solutions less dilute, or the time longer; further the results obtained by the "pipetting" method show, on the whole, fewer discrepancies than those obtained by the method of "filtration." In other words when the system is, by hypothesis, in a condition of strain, differences between the individual results are noticeable, but when the conditions favourable to production of such strain are removed, the discrepancies among the individual results tend also to disappear.

19. In paragraph 4 it was stated that the influence of water of dilution on the reaction between strontium chloride and sulphuric acid had been examined, but that the numbers obtained led apparently to no general results. We think that the great discrepancies noticed between the numbers obtained may be explained by the hypothesis already advanced. Sulphuric acid forms many hydrates with water, and is doubtless able to attach to itself large numbers of water molecules. If our hypothesis be true, we should expect a system containing sulphuric acid, much water, and such a salt as strontium chloride, to be in an eminently strained condition, and therefore to be capable of having its equilibrium upset by very small amounts of impressed force.

Now, unless very special precautions were taken to maintain the conditions of each experiment altogether unchanged during the whole course of that experiment, and unless a very delicate method of determining the amount of change, under given conditions, were adopted, we should expect to obtain discordant results. But we did not adopt such *special* precaution, nor was the method of measuring the amount of change characterised by extreme delicacy.*

The results obtained were therefore discordant, as indeed we should expect them to be if our hypothesis be correct. We subjoin a few of the actual numbers obtained.

* The method consisted in filtering a portion of the clear liquid, precipitating undecomposed strontium chloride as carbonate, dissolving in standard acid, and determining residual acid by titration with standard alkali.

PLATE VI. (TABLE X)
 Ba_2NO_3 and $\text{K}_2\text{C}_2\text{O}_4 = 1.1$ molecules
 "Pipelling" and "Filtration Curves"

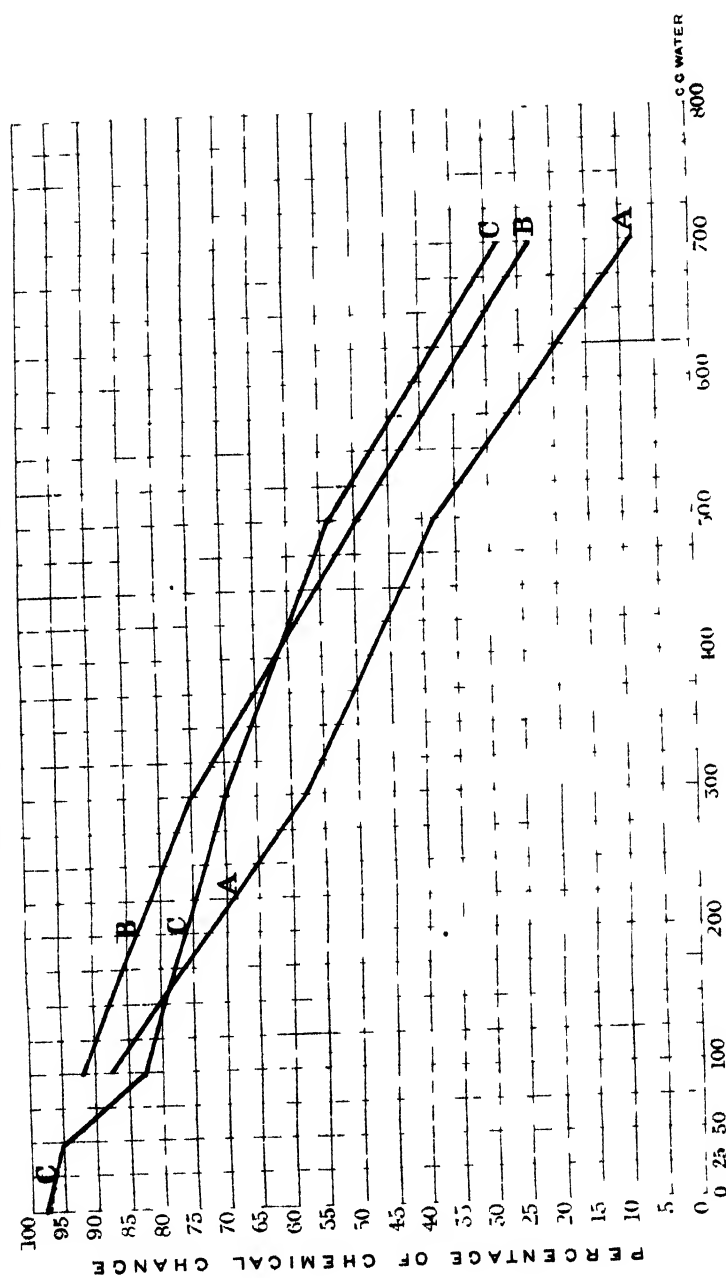


TABLE IX.—*Strontium Chloride and Sulphuric Acid.*

20 c.c. SrCl_2 solution used = 354.64 mgrms. SrCl_2 . 8.8 c.c. H_2SO_4 solution used = 877.52 mgrms. H_2SO_4 .

$\text{SrCl}_2 : \text{H}_2\text{SO}_4 = 1 : 4$ mols. Temp. = 16–18°.

c.c. water added.	Percentage of SrCl_2 decomposed.				
	Time = 60 mins.			Time = 18 hours.	
25	75.9	—	—	—	—
50	73.6	—	—	—	—
75	62.9	66.1	77.3	78.7	68.5
100	52.8	67.2	64.7	—	—
125	47.7	—	—	—	—
150	33.7	49.6	—	33.7	38.3
175	46.2	—	—	—	—
200	27.4	—	—	—	—
225	29.7	—	—	24.9	43.3
250	27.8	—	—	—	—

Time = 60 mins. $\text{SrCl}_2 : \text{H}_2\text{SO}_4 = 1 : 2.5$ mols.

25	70.1	67.5	85.5	—	—	—
50	74.5	60.4	56.4	—	—	—
90	52.0	53.0	—	—	—	—
100	49.5	51.7	55.1	—	—	—
125	45.2	51.1	39.4	50.2	46.0	54.4
150	36.9	22.5	21.5	32.2	—	—
175	14.2	24.8	10.6	—	—	—

20. As a further test of the value of our hypothesis, we carried out a short series of determinations of the influence of water of dilution on the change which occurs when barium nitrate is decomposed by means of potassium oxalate.

TABLE X.—*Barium Nitrate and Potassium Oxalate.*

Used 10 c.c. Ba_2NO_3 solution = 800 mgrms. Ba_2NO_3 , and 9.4 c.c.

$\text{K}_2\text{C}_2\text{O}_4$ solution = 509 mgrms. $\text{K}_2\text{C}_2\text{O}_4$.

$\text{Ba}_2\text{NO}_3 : \text{K}_2\text{C}_2\text{O}_4 = 1 : 1$ mols. *Pipetting.* Time = 90 mins.

c.c. water added.	Percentage Ba_2NO_3 decomposed.	
	3°.	18°.
100	85.4	91.8
300	58.4	76.4
500	39.4	50.3
700	9.1	25.3

Filtration (first 50 c.c.) results. Time = 90 mins. Temp. = 3°.

c.c. water added.	Percentage Ba ₂ NO ₃ decomposed.
0	98·7
25	96·9
50	95·8
100	83·0
300	70·5
500	53·0
700	29·5

These results are represented graphically in Curves A, B, and C, Plate VI.

The "pipetted" results show little or no indication of formation of hydrates: in the "filtered" results on the other hand such indication is clearly shown when the quantity of water of dilution becomes considerable.

21. We subjoin certain data taken from Guthrie's papers regarding the cryohydrates of the salts employed by us.

BaCl ₂ .2H ₂ O cryohydrate solidifies at	— 8°	with 37 mols. of water.
SrCl ₂ .6H ₂ O	„ „	—17° „ 23 „
CaCl ₂ .3H ₂ O	„ „	—37° „ 12 „
Ba ₂ NO ₃	„ „	— 0·8° „ 259 „
K ₂ C ₂ O ₄	„ „	+ 6·3° „ 17 „

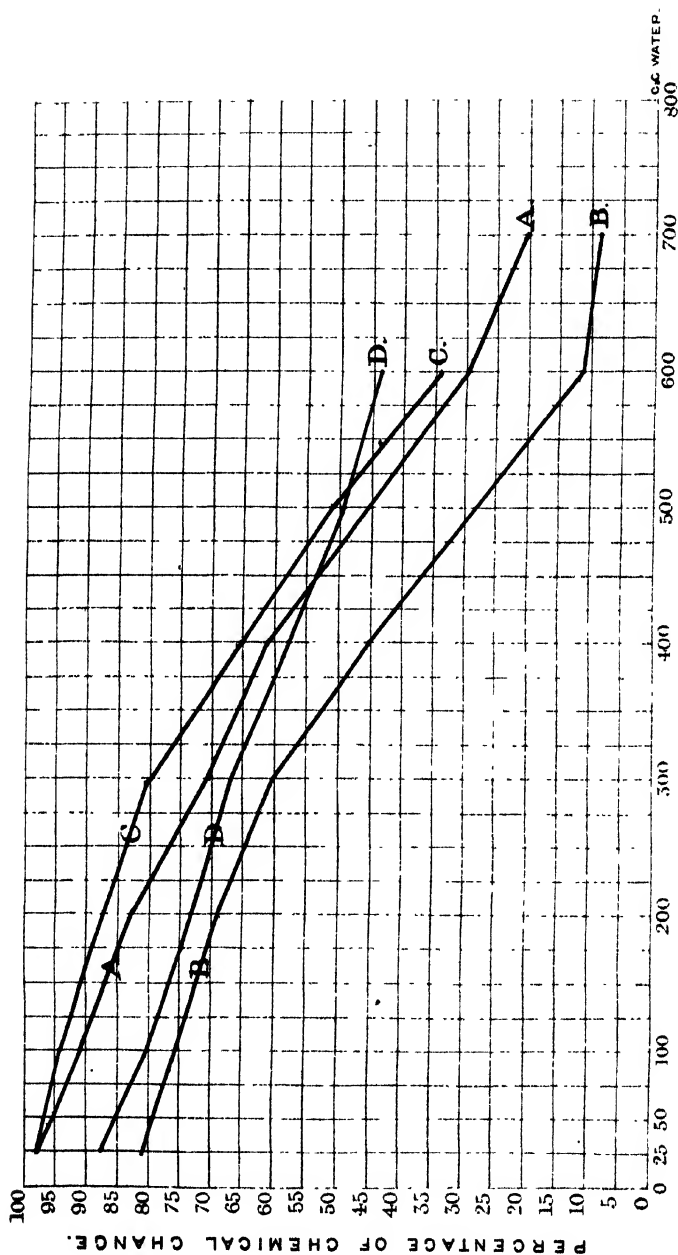
In the reaction in which calcium chloride was decomposed by addition of sodium carbonate, the influence of water of dilution on the change was regular; because, on our hypothesis, the tendency to formation of the cryohydrate of calcium chloride is but feebly marked under any experimental conditions realised by us. In the reaction between barium nitrate and potassium oxalate the influence of water of dilution is regular; because, the cryohydrate of barium nitrate tends to be formed in considerable quantity under the experimental conditions employed. But if the determinations of the amount of change are made in the filtered liquid, then the results show large differences from those obtained by the "pipetting" method; because, the equilibrium of the system, although sufficiently stable to resist overthrow by the mere process of pipetting off a portion thereof, is nevertheless disturbed by the process of filtration.

Further, the influence of water of dilution on the change which occurs when barium chloride and potassium oxalate mutually react, is irregular; because—on our hypothesis—the cryohydrate of barium chloride tends to be formed under the conditions of experiment, but not to be formed to such an extent as renders the system, comparatively, stable.

PLATE VII.

BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$. 1:1 molecules. - 3 and 18°.

Influence of Time.



A comparison of the "filtration" and "pipetted" curves for barium nitrate with those for barium chloride, under the same conditions of temperature and time (A and C, Plate VI, with C and B, Plate IV), shows that the difference between the results obtained by the two methods is much greater in the case of the nitrate than in that of the chloride.

On our view of the influence of water of dilution, the very stability of the barium nitrate solution (because of the large formation of cryohydrate) would be looked on as the reason why, when that stability is overthrown, the velocity of the chemical change is so largely increased.

22. But there is an aspect of the influence of water of dilution other than that which we have hitherto regarded.

The addition of much water might be supposed to bestow upon the reacting system a greater degree of molecular mobility than would be possessed by a more concentrated solution. Chemical change should therefore occur with greater readiness in the former than in the latter liquid. But at the same time the chances of molecular encounters, and therefore of molecular decompositions, occurring in unit time, must be smaller in dilute than in concentrated liquids, notwithstanding the greater mobility of the former system. Therefore we should conclude that the influence on the chemical change of small impressed forces would be more marked in dilute than in less dilute solutions, while at the same time the total amount of change under the same conditions would be greater in the more concentrated solutions.

Dewille (*Phil. Mag.* [4], 32, 365) has advanced a theory of the influence of dilution, in which he supposes that energy of position is actually gained by the reacting molecules when dilution is increased, and that this energy may be changed into mechanical work, whereby again heat may be evolved sufficient to raise some of the chemically active molecules present to their dissociation-temperature, *i.e.*, to shatter them into their constituent atoms.

But without pushing the influence of dilution so far as this, we think we are justified in supposing that in addition to the loss of energy involved in the formation of complex (cryohydrate) molecules, there would be a gain of mobility in the case of those molecules of the reacting bodies which had not thus associated to themselves large numbers of water molecules. Dilution would thus exert two, more or less opposing, actions.

The general result of a series of experiments, carried out by one of us,* is in keeping with the hypothetical deduction that impressed force should produce greater differences in the amount of chemical change when dilute, than when more concentrated solutions, are used.

* See next paper.

23. How should time influence the process of chemical change, specially studied by us, when taking place in dilute solutions, as compared with the influence of the same variable on the same change occurring in more concentrated solutions?

It is not easy to answer this question on *à priori* grounds. The influence exerted by time we should expect to vary, according as a low or a high temperature is maintained. At a low temperature formation of cryohydrate would tend to be increased by increasing time of action; but if dilution act by increasing molecular mobility, as well as by increasing formation of complex (cryohydrate) molecules, we should almost expect that the differences between the total amounts of change, in long, and in short, times, would be less in dilute, than in concentrated solutions.

In a tolerably concentrated solution at a low temperature we have, by hypothesis, a tendency to formation of cryohydrate molecules; water is added, and thereby the tendency aforesaid is increased, but simultancously molecular mobility is imparted to the system; the greater the amount of mobility the more rapidly will the chemical change proceed: in other words, in dilute solutions the chemical change will complete itself more rapidly than in less dilute solutions. Now if the tendency to formation of cryohydrate be small, *e.g.*, if temperature be somewhat high, the influence of time should probably be less marked than if the tendency to formation of cryohydrate be large.

The results already detailed are arranged in graphic form in Plate VII, with the view of illustrating the influence of time. Curves A and B, which represent results obtained at 3°, show little difference between the action of time in concentrated and in dilute solutions; but Curves C and D show that at a higher temperature (18°) the influence of time is less marked when much water of dilution is present.

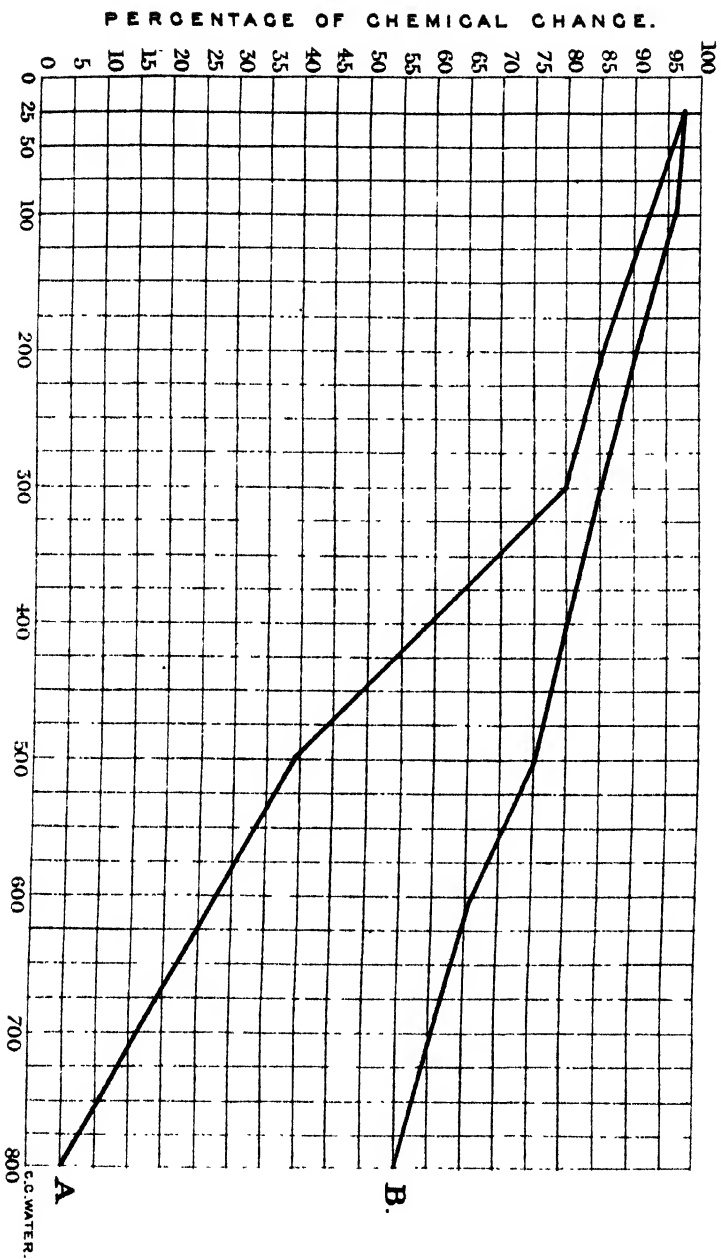
If, however, the difference between the times of action were made very considerable, the temperature being somewhat higher than that at which cryohydrate may be supposed to form rapidly, then we think that the curves representing the results at the two times should diverge largely. Now the curves of Plate VIII, representing results after 90 minutes (A), and after 5 hours (B) at 18°, diverge very largely.

The following table contains the results obtained for 5 hours' action at 18° by the pipetting method (Curve B of Plate VIII):—

PLATE VIII.

BaCl_2 and $\text{K}_2\text{C}_2\text{O}_4$, 1:1 molecules. - 18°.

Influence of Time.



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c.c. water added.	Mean percentage of BaCl ₂ decomposed.	Numbers actually obtained.	
50	97·6	97·6	97·7
100	95·6	95·6	95·6
300	85·2	85·5	84·9
500	75·7	77·4	74·1
700	59·3	60·4	58·1
900	44·7	44·7	—
1100	18·7	18·3	19·1

24. Every chemical system appears to tend towards that condition of equilibrium, the attainment of which is marked by the greatest loss of energy. It may, perhaps, be more correct to say that the entropy of chemical systems, *i.e.*,—that portion of the energy, which, being dependent on the configuration of the parts of the system, is available as mechanical energy,—continually tends to become less.

This tendency to dissipation of energy may be arrested in various ways, among others by impressing upon the system what may perhaps be described as an artificial state of equilibrium.

Thus, the condition of most stable equilibrium for a system originally consisting of barium chloride and potassium oxalate molecules, would be that in which barium oxalate and potassium chloride molecules are produced, but by adding much water a portion of the reacting molecules are, by our hypothesis, loaded with water of hydration. In this loading energy is lost, but less energy than would be lost by the formation of molecules of potassium chloride and barium oxalate; the system is therefore in an unstable condition, but a certain degree of stability is impressed upon it by the presence of a large mass of one of the products of dissociation of the complex and unstable hydrated molecules.

We have thus a system in a state of strain because of the stress between its parts. A small force may be sufficient to relieve the strain, and this relief may be attended with a rapid rearrangement of the parts of the system, and with a large decrease in the entropy of the system.*

25. If the state of the system which we have endeavoured to picture in the foregoing sentences be at all correspondent with the actual state of the system, we should expect small differences in physical conditions to produce much greater variations in the amount of chemical change, in dilute, than in more concentrated solutions.

The following results are in keeping with this supposition:—

* We seem to have here an action opposed to that designated "chemical induction," by Bunsen and Roscoe (*Phil. Trans.*, 1857). The state of a system of heterogeneous molecules capable of mutual chemical action is compared by these chemists to that

TABLE XI.—*Pipetting.*

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 = 1 : 1$ mol. Temp. = 20° . Water of dilution = 1100 c.c.

	Percentage of BaCl_2 decomposed.					
	Time = 5 hours.			Time = 28 hours.		
			Diff.			Diff.
Roughened beaker ..	31.2	34.8	3.8	67.8	66.3	1.5
Broken glass in beaker	9.7	39.8	30.1	66.3	60.6	5.7
Oxalate added with constant stirring....	11.0	37.0	26.0	67.1	59.9	7.2
Oxalate added on surface; after 15 minutes whole stirred up....	14.0	39.1	25.1	62.7	62.1	0.6

Temp. = 20° . Time = 90 mins.

	Percentage of BaCl_2 decomposed.					
	Dilution = 800 c.c.			Dilution = 700 c.c.		
			Diff.			Diff.
Roughened beaker ..	1.5	3.5	2.0	24.3	21.7	2.6
Broken glass in beaker	1.0	3.0	2.0	7.0	11.0	4.0
Oxalate added with constant stirring....	6.8	3.8	3.0	22.4	16.5	5.9
Oxalate added on surface; after 15 minutes whole stirred up....	3.0	1.0	2.0	11.1	11.1	0.0

Temp. = 20° . Water of dilution = 700 c.c.

	Percentage of BaCl_2 decomposed.					
	Time = 90 mins.			Time = 24 hours.		
			Diff.			Diff.
Roughened beaker ..	24.3	21.7	2.6	81.6	—	—
Broken glass in beaker	7.0	11.0	4.0	79.3	—	—
Oxalate added with constant stirring....	22.5	16.5	5.9	79.3	81.1	1.8
Oxalate added on surface; after 15 minutes whole stirred up....	11.1	11.1	0.0	79.3	—	—

of a wire with a certain weight attached; induction tends to remove the weight. But the addition of water to the system considered by us tends to increase this weight, and so to elongate the wire. Remove the weight, however, and the wire suddenly contracts.

Time = 30 mins.

	Percentage of BaCl ₂ decomposed.	
	Temp. = 20°.	Temp. = 70°.
Dilution = 800 c.c...	0·0	1·0
„ = 700 c.c...	3·7	33·7

(See also curves of Plate VII.)

26. From these results it is apparent that physical differences affect the total amount of chemical change when much water of dilution is present and the time of action is moderately short (*see 700 c.c. 90 minutes*). Further, that if the amount of dilution-water is made very large, the differences between the results obtained become immense, showing how the action is disturbed by very small alterations in physical conditions (*see 1100 c.c. 5 hours*). But that, if the time of action be prolonged, the results become tolerably concordant, and that those physical conditions which were made the subject of examination, but slightly affect the final amount of chemical change, when that change is allowed to proceed for prolonged periods, even when in exceedingly dilute liquids (*see 1100 c.c. 28 hours, and 700 c.c. 24 hours*).

Further, we conclude from these numbers that, if the amount of water of dilution be so large, and the time of action be such, that but a very small amount of chemical change ensues, then the amount of that change is only slightly affected by the changes in physical conditions to which the liquids were subjected in our experiments (*see 800 c.c. 90 minutes*).

The results of Table XI, bearing upon the influence of temperature corroborate those of par. 22, viz., that in dilute solutions rise of temperature largely increases the amount of chemical change: the experiments made with 800 c.c. of water of dilution, however, show that, if the amount of change at a moderate temperature be almost nothing, a rise of temperature scarcely affects the total decomposition.

27. We think that the experiments recorded in the present paper justify our general hypothesis, viz., that the amount of chemical change which occurs when barium chloride and potassium oxalate are mixed in the proportion of 1 : 1 molecules, is irregularly affected by variations in the mass of water of dilution present, because the entire system is brought into a state of strain due to the stress between its parts; and that the principal forces of which this stress is compounded, are, the force tending to produce cryohydrate—and other hydrated—molecules the force tending to split up these molecules, and the force tending to separate, and so to impart greater mobility to, the chemically active molecules of the system.

The results which we have obtained are, it seems to us, corrobora-

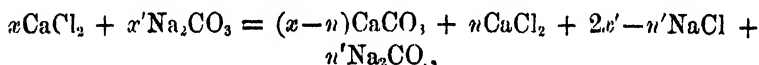
tive of what may be called "the kinetic theory of chemical action," viz., that systems apparently stable are continually undergoing atomic interchanges.

We have spoken of a system of chemically active molecules as being, under certain conditions, in a state of strain; we believe that analogies with this state may be found in supersaturated solutions,* colloidal molecules,† and that "particular condition of bodies in which they are the *débris* of some compound, and not proper chemical compounds of their constituents."‡

No. IV.—*On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution.*

By M. M. PATTISON MUIR.

1. The influence of temperature upon the reaction formulated as—



was considered in outline in the first of these contributions (*loc. cit.*).

The general result, deducible from the curves of Table G in that paper, is, that the amount of chemical change in unit time increases as the temperature is varied, and this more rapidly with the earlier than with the later increments of temperature.

The initial state of the chemical system in these experiments was approximately $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 1,500$ mols.

If more concentrated solutions be employed, the influence of temperature is less marked: this is shown by the following numbers:—§

* See especially Tilden, "Theory of Solution, &c.," a lecture delivered to the Bristol Naturalists' Society, Feb., 1878.

† "Liquid Diffusion applied to Analysis." *Phil. Trans.*, 1861.

‡ "On Hydrated Salts and Metallic Peroxides," by Graham; *Brit. Assoc. Reports*, 1834.

§ The numbers given are all the means of at least two closely agreeing experiments.

PLATE IX. (TABLE XIII).

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 = 1:1$ molecules. 30 minutes.

Influence of Temperature.

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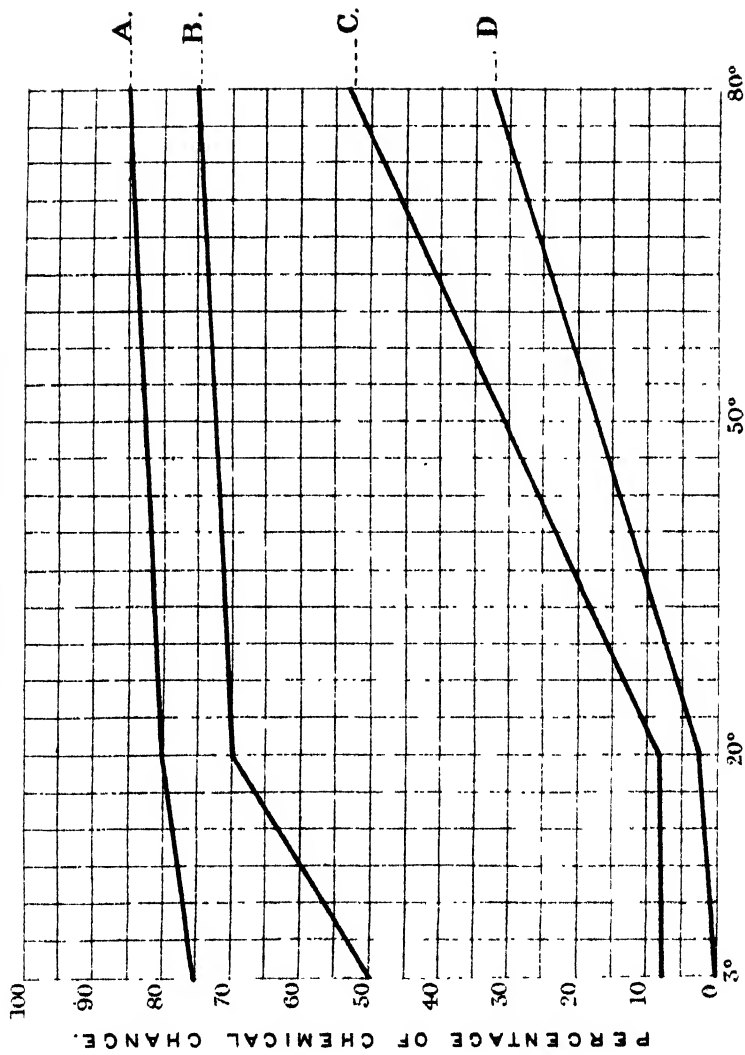


TABLE XII.

10 c.c. calcium chloride solution used = 320.27 mgrms. CaCl_2 + 8.1 c.c.
 sodium carbonate solution = 305.54 mgrms. Na_2CO_3 .
 Initial condition = $\text{CaCl}_2 : \text{Na}_2\text{CO}_3 : \text{H}_2\text{O} = 1 : 1 : 330$ mols.
 Each 25 c.c. water added = 470 mols. Time = 10 mins.

Water added. c.c.	Mean percentage of CaCl_2 decomposed.		
	20°.	50°.	80°.
50	89.1	89.4	89.6
100	85.5	83.5	88.2
250	83.8	89.0	88.8
Time = 60 mins.			
50	91.2	91.4	94.6
100	90.3	91.9	94.2
200	87.9	89.3	—
300	85.2	87.2	—
500	72.6	77.6	82.9

Several other series of experiments were carried out with a similar result, viz., that temperature exerts little influence on the course of the change, except when somewhat dilute solutions are employed, and that the influence is then regular.

In place of continuing these experiments with much more dilute solutions, as was originally intended, I determined to examine in a little more detail the influence of temperature on the reaction between barium chloride and potassium oxalate, as from the results contained in the preceding paper, facts of more general interest might reasonably be expected from this study.

2. The solutions used and the experimental methods employed were the same as those described in the preceding paper.

TABLE XIII.

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 : \text{H}_2\text{O} = 1 : 1 : 360$ mols.
 Each 100 c.c. water added = 1840 mols. Time = 30 mins.

c.c. water added.	Mean percentage of BaCl_2 decomposed.			Numbers actually obtained.				
	3°.	20°.	80°.	3°.	20°.	80°.		
100	74.8	79.8	85.0	74.8	—	79.8	—	85.0
300	51.1	70.8	76.0	50.1	52.2	73.2	68.5	75.7
600	7.8	8.3	51.1	7.8	—	8.9	7.8	52.0
700	1.0	3.7	33.7	1.0	—	3.7	—	33.7

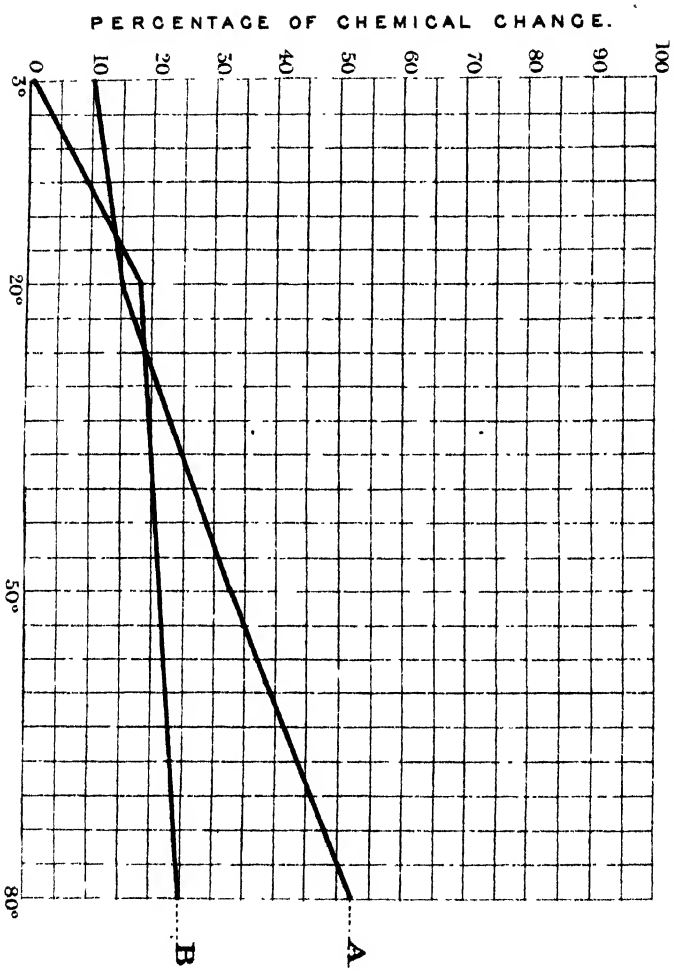
Curves A, B, C, and D of Plate IX represent these results in graphic form.

PLATE XI. (TABLE XV.)

$\text{BaCl}_2 \cdot \text{K}_2\text{C}_2\text{O}_4 \cdot 1$:2 molecules. 30 minutes.

Influence of Temperature.

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3. Curves A and B (100 c.c. and 300 c.c. water) confirm the results of the experiments with calcium chloride and sodium carbonate.

The influence of temperature begins to be felt when 300 c.c. water of dilution are added; the increase in the amount of chemical change is considerably greater for the rise of temperature from 3° to 20° than for that from 20° to 80° .

But when 600 c.c. and 700 c.c. of water are added (Curves C and D), a different result is observed. The increase in the amount of chemical change is very small for the first rise of 20° , but after that the increase is rapid.

These results are, I think, explicable in terms of the "*strain hypothesis*," developed in the preceding paper. With tolerably dilute solutions, where the formation of cryohydrate molecules is (by hypothesis) small, a moderate increase of temperature is accompanied by a considerable increase in the amount of chemical change; but the system having now very nearly reached the point of most stable equilibrium, further increase of temperature exerts but little influence on the amount of change. If, however, the conditions favourable to formation of hydrated molecules be maintained—much water and low temperature—then a (comparatively) small rise of temperature does not succeed in thoroughly decomposing the loaded molecules. When, however, this decomposition is effected, the chemical change proceeds at an accelerated rate, *i.e.*, when the change is fairly started the curves rapidly ascend.

It is probable that as the point of maximum stability of the system is approached, the influence of temperature on the change would become less and less marked, in other words, the curves would again approach straight lines; if this were so, the curves would exhibit points of contrary flexure.

4. Experiments were now conducted similar to those of Table XIII, except that the time was made 90 minutes (see p. 80).

5. The higher curves of Plate X exhibit the contrary flexure referred to in the last paragraph: but this again disappears when *very* dilute solutions are employed.

Generally, then, it may be said that with concentrated solutions, temperature exerts little influence on the amount of the change under consideration: with more dilute solutions, the first increase of about 20° causes a marked increase in the amount of change, but after this influence of temperature is more regular: with yet more dilute solutions, increase of temperature causes at first a slight increase in the amount of chemical action, but as the temperature continues to rise, the amount of action rapidly increases, until a point is reached after which further increase of temperature but slightly affects the amount of chemical change: and finally, that with *very* dilute solutions the

influence of temperature again becomes nearly regular, the points of contrary flexure being higher up in the curves, and being very much less marked, the curvature of the curves being smaller.

6. A few experiments were carried out in order to determine the effect of increasing the mass of one of the reacting substances.

TABLE XV.

$\text{BaCl}_2 : \text{K}_2\text{C}_2\text{O}_4 : \text{H}_2\text{O} = 1 : 2 : 340$ mols.

Details as before. *Pipetting.* Time = 30 mins.

c.c. water added.	Mean percentage of BaCl_2 decomposed.				Numbers actually obtained.			
	3°.	20°.	50°.	80°.	3°.	20°.	50°.	80°.
800	10.5	16.0	34.0	53.2	10.5	16.0	34.0	51.4 55.1
1000	2.5	18.0	—	24.0	2.5	19.0	17.0	— : 23.0 25.0

7. These results (see Curves A and B of Plate XI) show, that with 2 mols. potassium oxalate to 1 mol. barium chloride and 800 c.c. water of dilution, the effect of increasing temperature upon the amount of chemical change is nearly, if not altogether, regular; but that in a more dilute solution (1000 c.c. water) the effect is similar to that in much less dilute solutions when equal mols. are used, *i.e.*, the first increase of 20° causes a much larger increase in the amount of change than either of the succeeding increments of 30°.

There is, however, in the Curve B no indication of contrary flexure, similar to that of Curves B to H of Plate X.

Let the action be fairly started, then the strained condition is, so to speak, neutralised by the effect of increased mass of potassium oxalate.

8. These experiments, I think, present certain points of analogy with the so-called "*induction*" of Bunsen and Roscoe.

We seem to have certain conditions under which the chemical change proceeds at the normal rate; but by altering these conditions, the rate of change may be accelerated or diminished. If the conditions which diminish the rate of change be somewhat suddenly removed, the change may be abnormally accelerated for a time, after which it may again return to its normal rate.

The conditions which accelerate or diminish the rate of change will probably vary for each chemical reaction: in the present case, dilution and temperature exert opposing actions on the change considered.

VII.—On α - and β -Phenanthrene-carboxylic Acids, with Remarks on the Constitution of Phenanthrene.

By FRANCIS R. JAPP, M.A., Ph.D., Assistant in the Chemical Research Laboratory, Science Schools, South Kensington.

I HAVE already described (*Ber.*, **10**, 1661), in conjunction with Dr. Schultz, a phenanthrene-carboxylic acid melting at 260° . I have since prepared this acid in greater quantity, and having thus been enabled to purify it more thoroughly, find that it melts at 266° . I now propose to designate it as α -phenanthrene-carboxylic acid, in order to distinguish it from the isomeride described for the first time in the present paper.

α -Phenanthrene-carboxylic acid was obtained from crystallised calcium phenanthrene-sulphonate by converting the latter into the sodium salt, distilling the dry sodium salt with potassic ferrocyanide, and saponifying the nitrile thus obtained.

In preparing the calcium phenanthrene-sulphonate, there was always a relatively small yield of crystallisable salt, and a considerable quantity of dark-coloured syrupy mother-liquor. This latter had been from time to time reserved for investigation.

As it seemed possible that this mother-liquor might contain an isomeric calcium phenanthrene-sulphonate, I determined to subject it to the same processes which had yielded a phenanthrene-carboxylic acid from the crystallised salt, hoping that the corresponding phenanthrene-carboxylic acid might be more easily purified than the syrupy sulphonate.

On adding sodium carbonate until the solution was alkaline, a copious precipitate of calcium carbonate was formed, denoting the presence of a very soluble calcium salt. The filtered solution of the sodium salt was evaporated to dryness, and the dried salt was mixed with one and a half times its weight of potassium ferrocyanide, and distilled in portions of 100 grams at a time from a flat copper retort. The nitrile thus obtained was a yellow, transparent, viscid liquid, which after standing for some days assumed a buttery consistency, probably owing to the presence of regenerated phenanthrene. It was saponified with alcoholic potash, and required boiling for over 100 hours with inverted condenser before ammonia ceased to be evolved. The alcohol was then distilled off, and the contents of the flask, after digesting with water, were diluted and filtered. On acidifying with hydrochloric acid, the new acid separated out as a dirty white flocculent precipitate. The yield of crude acid from 2 kilos. of commercial phenanthrene was only 80 grams.

The purification of this acid presented considerable difficulties. It dissolved in ammonia, yielding a brown liquid. On adding an excess of barium chloride, the barium salt was precipitated, carrying with it most of the resinous colouring matters. On boiling, the barium salt went partly into solution, yielding a nearly colourless liquid, which was filtered hot from the impurities. The residue had to be repeatedly extracted with boiling water, as the impurities enclosed the salt and rendered its solution difficult.

Subsequent experience with the barium salt has shown that a repeated recrystallisation of this salt would probably have offered a good means of purifying the acid, but at this stage the salt did not seem to promise well, and its use was abandoned. After a trial of several salts, the sodium salt, which crystallised in long rhomboidal laminæ with a slight satiny lustre, was selected. The salt was recrystallised several times until it was quite colourless. On adding hydrochloric acid to the solution, β -phenanthrene-carboxylic acid was obtained as a white flocculent precipitate.

β -Phenanthrene-carboxylic acid is soluble in alcohol, ether, and glacial acetic acid, almost-insoluble in water. From a hot saturated acetic acid solution it crystallises in stellate groups of colourless needles. It sublimes in fern-shaped leaves, exactly resembling those of the α -acid. It melts at 250—252°. Analysis yielded the following results:—

I. 0.2268 gram gave 0.6765 gram carbonic anhydride and 0.0938 gram water.

II. 0.2837 gram gave 0.8452 gram carbonic anhydride and 0.1151 gram water.

	Calculated for $C_{15}H_{10}O_2$.		Found.	
			I.	II.
C_{15}	180	81.08	81.36	81.23
H_{10}	10	4.50	4.59	4.51
O_2	32	14.42	(14.05)	(14.26)
	222	100.00	100.00	100.00

A determination of water of crystallisation and sodium in the sodium salt above referred to gave the following results:—

0.3782 gram (of a preparation which had been exposed to the air for a long time) lost on heating to 140° 0.0986 gram, and the remaining 0.2796 gram anhydrous salt when treated with concentrated sulphuric acid and heated to redness, gave 0.0798 gram sodium sulphate.

The formula $C_{15}H_9.CO_2Na + 5H_2O$ requires 26.96 per cent. H_2O . Found 26.07.

The formula $C_{14}H_9.CO_2Na$ (anhydrous) requires 9.43 per cent. Na. Found, 9.25.

The barium salt was obtained as a crystalline precipitate when barium chloride was added to a solution of the sodium salt. It was purified by recrystallising from a hot aqueous solution, and formed colourless branched needles, which under the microscope appeared as long rectangular laminæ. These laminæ were very brittle, and possessed a cleavage parallel to the right angled termination. Water of crystallisation and barium were determined, with the following results:—

I. 0.3765 gram air-dried salt lost on heating to 140° 0.0582 gram, and the remaining 0.3183 gram anhydrous salt gave 0.1276 gram barium sulphate.

II. 0.3185 gram lost on heating to 140° 0.0490 gram, and the remaining 0.2695 gram anhydrous salt gave 0.1070 gram barium sulphate.

The formula $(C_{14}H_8.CO_2)_2Ba + 6H_2O$ requires 15.71 per cent. H_2O . Found—I. 15.45; II. 15.38.

The formula $(C_{14}H_8.CO_2)_2Ba$ (anhydrous) requires 23.66 per cent. Ba. Found—I. 23.57; II. 23.34.

Distillation of β -Phenanthrene-carboxylic Acid with Soda-lime.

In order to prove that the acid was really a derivative of phenanthrene, 8 grams of the sodium salt were distilled with soda-lime. The phenanthrene thus obtained was identified by its melting point, by that of its picric acid double compound, and, lastly, by that of the quinone prepared from it by oxidation. The other physical properties of these compounds agreed perfectly with those of the phenanthrene compounds in question. Furthermore, the quinone dissolved without residue in a solution of acid sodium sulphite.

Oxidation of β -Phenanthrene-carboxylic Acid.

1 gram of the acid was oxidised with about twice its weight of chromic anhydride in acetic acid solution. On distilling off the excess of acetic acid and diluting with water, a substance was precipitated in orange-yellow needles, from which a solution of sodium carbonate extracted a small quantity of unoxidised phenanthrene-carboxylic acid. The residue dissolved almost entirely in a solution of acid sodium sulphite. The pure substance reprecipitated from this solution was crystallised once from glacial acetic acid, and was thus obtained in orange-yellow needles melting at $204-204.5^{\circ}$. (M. p. of phenanthrene-quinone given by Fittig at 198° , found by myself on a very pure specimen as high as 206° .)

Analysis yielded the following results:—

0.1924 gram gave 0.5682 gram carbonic anhydride and 0.0711 gram water.

	Calculated for $C_{14}H_9O_2$.		Found.
C_{14}	168	80.77	80.51
H_9	8	3.85	4.10
O_2	32	15.38	(15.39)
	208	100.00	100.00

The substance was therefore pure phenanthrene-quinone.

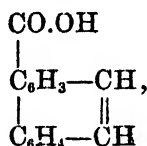
Tubulated Comparison of α - and β -Phenanthrene-carboxylic Acids.

The following table contains the result of a comparison of the two phenanthrene-carboxylic acids and their sodium and barium salts. Most of the crystallographical characteristics here described can be perceived only with the aid of a microscope:—

	α -Acid.	β -Acid.
Acid.....	Crystallises from hot glacial acetic acid in colourless, curved blades, with parallel edges, and a rectangular termination. This curvature is very characteristic. Sublimes in fern-shaped leaves. M. p. 266°. (The melting point 260° was given in the first paper.)	Crystallises from hot glacial acetic acid, in stellate groups of colourless, straight, pointed needles. Sublimes in fern-shaped leaves. M. p. 250—252°.
Sodium salt..	$C_{14}H_9.CO_2Na + 4H_2O$. Tufts of colourless, pointed blades. 100 parts of water at 20° dissolves 6.8 parts of the anhydrous salt. Almost indefinitely soluble in boiling water.	$C_{14}H_9.CO_2Na + 5H_2O$. Colourless, rhomboidal laminæ, with a slightly satiny lustre. 100 parts of water at 20° dissolve 6.2 parts of the anhydrous salt. Almost indefinitely soluble in boiling water.
Barium salt..	$(C_{14}H_9.CO_2)_2Ba + 7H_2O$. Colourless, long needled of extraordinary fineness and flexibility, radiating from one point to form large balls or tufts. Under the microscope a tangled mass of these flexible needles has the appearance of vegetable fibre. 100 parts of water dissolve— At 20°.. .066 } part of anhy- „ 100°.. .560 } drous salt.	$(C_{14}H_9.CO_2)_2Ba + 6H_2O$. Colourless, long, brittle, rectangular laminæ, united in a ramiform crystallisation. 100 parts of water dissolve— At 20°.. .27 } parts of anhy- „ 100°.. 3.70 } drous salt.

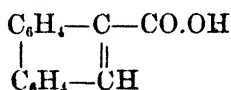
Theoretical Considerations.

It has been shown (Japp and Schultz, *loc. cit.*) that α -phenanthrene-carboxylic acid yields on oxidation phenanthrene-quinone-carboxylic acid, the carboxyl group remaining intact, and that α -phenanthrene-carboxylic acid has therefore the formula—

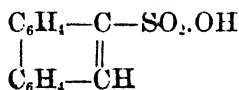


the exact position of the carboxyl group in the benzene nucleus remaining undetermined.

A phenanthrene-carboxylic acid which on oxidation yields phenanthrene-quinone, with elimination of the carboxyl group, must contain this group attached to one of those carbon atoms which in the quinone are united with quinonic oxygen. This would give—



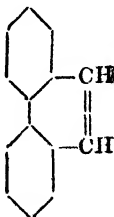
as the constitutional formula of β -phenanthrene-carboxylic acid,* and—



as the formula of the sulphonic acid from which it is derived, supposing no migration of atoms within the molecule to have taken place during the distillation with potassic ferrocyanide.†

The formation of this sulphonic acid by the direct action of concentrated sulphuric acid on phenanthrene seems to me to cast fresh light on the constitution of phenanthrene, and indirectly on that of the benzene nucleus.

The graphic formula of phenanthrene, expressed in terms of Kekulé's benzene theory, is—



* Liebermann and vom Rath (*Ber.*, 8, 248) seem to have observed the presence of this acid as an impurity in their anthracene-carboxylic acid. They mention that a specimen of the latter acid, prepared from impure anthracene, yielded on oxidation, in addition to anthraquinone-carboxylic acid, phenanthrene-quinone.

† As this point was of importance, the following experiment was undertaken to decide it:—A portion of the very soluble sodium phenanthrene-sulphonate, from which the β -phenanthrene-carboxylic acid was prepared, was dissolved in water, and oxidised with a mixture of potassium dichromate and sulphuric acid. Carbonic

a plain hexagon being employed to symbolise the benzene nucleus in order to avoid introducing the complicated question of alternate double and single bonds, to which, however, reference will be made further on.

Graebe's synthesis of this compound from stilbene—symmetrical diphenyl-ethylene—shows it to be diphenylene-ethylene. Schultz (*Ber.*, **11**, 215), on the one hand, and Anschuetz and Japp (*ibid.*, **11**, 211), on the other, showed by two independent methods that phenanthrene is a diortho-compound, and that it must therefore be regarded as symmetrical diortho-diphenylene-ethylene, as expressed in the above graphic formula.

Many of the chemical reactions of phenanthrene seem to indicate that the dyad ethylene residue $-\text{CH}=\text{CH}-$ in the diphenylene-ethylene forms part of an aromatic nucleus. On oxidation the two atoms of hydrogen are replaced by *two* atoms of oxygen (not by one), a quinone being formed. This quinone on reduction yields a hydroquinone containing the group $-\text{C}(\text{OH})=\text{C}(\text{OH})-$, and dissolving in caustic alkalis by virtue of these phenylic hydroxyl groups. Monobromphenanthrene, in which the substitution of bromine takes place in the $-\text{CH}=\text{CH}-$ group—the compound yielding on oxidation phenanthrene-quinone with elimination of the bromine atom—may, as Anschuetz has shown (*Ber.*, **11**, 1217), be heated with strong alcoholic potash to 170° without undergoing change. Anschuetz points out the bearings of this fact, and the importance of a proof of the aromatic character of this portion of the phenanthrene molecule. Indeed, when one considers the relative mobility of the bromine atom in monobromethylene and monobromstilbene, when these compounds are heated with alcoholic potash, this stability of monobromphenanthrene must be allowed to furnish very strong evidence that the group $-\text{CH}=\text{CH}-$ forms part of an aromatic nucleus.

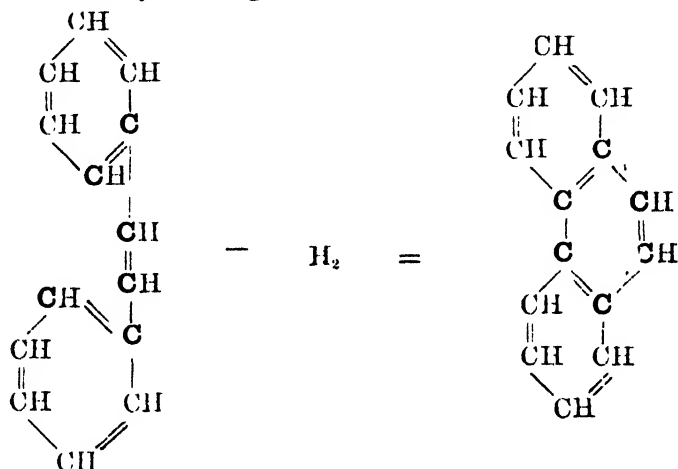
A fresh piece of evidence of a similar character may be found in the above-described direct formation from phenanthrene and sulphuric acid of a sulphonic acid, in which the sulphonic group replaces one of the hydrogen atoms of the $-\text{CH}=\text{CH}-$ group. A direct sulphonation of a hydrocarbon has as yet been observed only in the aromatic nucleus. In the fatty series the presence of an electro-negative group (CN, CO.OH, &c.) is necessary, in order that direct sulphonation may take place.

These reactions are without exception specifically aromatic in

anhydride was evolved, and an orange-yellow precipitate was formed, which, after purifying in the manner already described (see "Oxidation of β -Phenanthrene-carboxylic Acid," p. 85), crystallised in needles, fusing between 198° and 200° , and exhibiting all the other properties of phenanthrene-quinone. The presence of a phenanthrene-sulphonic acid of the above formula was thus proved.

character, and, taken together, form a strong cumulative proof that the $-\text{CH}=\text{CH}-$ group belongs to a benzene nucleus.

In the synthesis of phenanthrene from symmetrical diphenyl-ethylene we have, therefore, constructed a benzene nucleus from the ethylene residue $-\text{CH}=\text{CH}-$ on the one hand (which, as long as it existed in diphenyl-ethylene, showed by its entire behaviour that it did not belong to a benzene nucleus) and, on the other, two pairs of carbon atoms, each of which pairs was contained in the ortho-position by a separate already existing nucleus:—



Phenanthrene, therefore, consists of three benzene nuclei, one of which shares four adjacent carbon atoms with the two others—one ortho-pair with each. Phenanthrene may thus be derived from naphthalene by a repetition of the process by which the latter hydrocarbon is derived from benzene—a suggestion thrown out by Graebe (*Ann. Chem. Pharm.*, **167**, 133) in his memoir on phenanthrene.

The portion of the hydrocarbon to the right of the dotted line in the above graphic formula is the dyad group to which reference has been made.

Ladenburg has shown (*Theorie der aromatischen Verbindungen*) that only two graphic formulæ satisfy the conditions required by a benzene nucleus—his own "prismatic" formula, and Kekulé's hexagon with alternate double and single bonds, or, what is practically identical with this latter, Lothar Meyer's modified Kekulé's hexagon with six free affinities. If the central nucleus in phenanthrene is a benzene nucleus, then Ladenburg's prism must be abandoned, as it is impossible to arrange three such prisms with four carbon atoms in the ortho-position in common, so as to satisfy the conditions required by the phenanthrene formula.*

* It is equally impossible to express the naphthalene formula by means of Laden-

As regards the formerly much vexed question of alternate double and single bonds in the benzene nucleus, and whether the ortho-compounds 1 : 2 and 1 : 6 ought on such a supposition to be identical, this difficulty could perhaps be best avoided by the adoption of Lothar Meyer's hexagon with six free affinities. Carried to its logical conclusion, this would lead to the universal substitution of free affinities for double bonds, as has been done before now. As long as we have no physical conception of what a bond is, this would involve no contradiction. All that a double bond represents is the potentiality of taking up two monad atoms or groups, and this is equally well accounted for by the assumption of free affinities. It is strange that in an open chain a double bond should represent the weakest part of the chain.

A final proof of the aromatic nature of the central nucleus of phenanthrene would be the preparation of naphthalene, or one of its derivatives, from this hydrocarbon. Experiments which I have made in this direction have as yet failed, owing to the oxidisable character of the central group, which causes it to be attacked sooner than the lateral nuclei, even when the hydrogen atoms of one of the latter have been replaced by hydroxyl groups in order to render the nucleus less stable.

It is evident from the graphic formula that five mono-substitution compounds of phenanthrene are theoretically possible.

VIII.—*On some Derivatives of Phenylacetic Acid.*

By P. PHILLIPS BEDSON, D.Sc., Assistant Lecturer and Demonstrator in Chemistry at the Owens College.

FOR our knowledge of the derivatives of phenylacetic acid we are chiefly indebted to Radziszewski (*Ber.*, 2, 207), who first investigated the conditions under which substitution may take place either in the aromatic nucleus or in the side-chain. My investigation of some of the derivatives of this acid has led to results differing somewhat from those of the above-mentioned chemist. I here propose to give an account of these results, together with some further particulars relative to the bromonitrophenylacetic acids, &c., the study of which I undertook, whilst in Bonn, at the proposal of Professor Kekulé, and burg's prism, but Ladenburg throws doubts on Graebe's proof of the symmetrical character of naphthalene.

short notices of which have already appeared in another Journal (*Ber.*, 10, 530 and 1657).

Nitro-derivatives.—Phenylacetic acid when nitrated yields two isomeric nitro-derivatives, viz., the para- and the ortho-, the former constituting the chief portion of the yield. The method of separating these two acids by the different solubilities of their barium salts, does not give satisfactory results. If, however, the acid prepared from the less soluble salt be crystallised repeatedly from a hot mixture of alcohol and water, an acid is obtained, crystallising in long needles, and melting at 150—151°, which proves to be paranitrophenylacetic acid.

(1.) *Paranitrophenylacetic acid* is soluble in hot water, from which it crystallises in long, yellowish-white, brittle needles; it is sparingly soluble in cold water, and easily in alcohol and ether. Its analyses gave the following results:—

I. 0.3066 gram yielded 0.5378 gram CO₂, and 0.1109 gram H₂O.

II. The “NO₂” was determined by Limpricht’s method (*Ber.*, 11, 35), 10 c.c. of stannous chloride solution diluted to 250 c.c. gave a solution, 10 c.c. of which required 10.83 c.c. of iodine solution. 1 c.c. of iodine solution contained 0.01108 gram I = 0.000667 gram NO₂. 0.2132 gram of acid heated with 10 c.c. SnCl₂ solution, diluted to 250 c.c., gave a solution 10 c.c. of which required 7.64 c.c. of iodine.

$$25 \times (10.83 - 7.63) \times 0.000667 = 0.005336 \text{ gram NO}_2.$$

			Found.	
			I.	II.
C ₈	=	96 53.03	53.16	—
H ₇	=	7 3.86	4.01	—
NO ₂	=	46 25.41	—	25.02
O ₂	=	32 17.67	—	—

181 100.00

This acid, when oxidised by a mixture of potassium bichromate and sulphuric acid, yielded paranitrobenzoic acid, m. p. 230°; the combustion of which gave the following numbers:—

0.3064 gram yielded 0.5682 gram CO₂ and 0.088 gram H₂O.

	Calculated for C ₆ H ₄ NO ₂ CO ₂ H.	Found.
C.....	50.29	50.52
H	2.99	3.16

Methyl paranitrophenylacetate, C₈H₄.NO₂.CH₂CO₂CH₃, crystallises from alcohol in yellowish-white plates, by slow evaporation of the alcoholic solution it is obtained in thick striated plates; it melts at 54—55°.

Ethyl paranitrophenylacetate crystallises from dilute alcohol in thin, shining leaflets, melting at 62—64°.

The *barium salt* is obtained in beautiful light yellow transparent crystals by allowing the aqueous solution to evaporate slowly. These crystals appear to be six-sided plates; as on exposure to air they effloresce and become opaque, their exact crystalline form could not be determined. The crystals quickly dried between filter-paper, gave results (I) corresponding to the formula $\text{Ba}(\text{C}_8\text{H}_6\text{NO}_4)_2 + 7\text{H}_2\text{O}$; whilst the air-dried opaque crystals gave results (II) for the formula $\text{Ba}(\text{C}_8\text{H}_6\text{NO}_4)_2 + 2\text{H}_2\text{O}$.

I. 0.5358 gram heated at 110—115° lost 0.113 gram, and gave 0.1959 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_8\text{H}_6\text{NO}_4)_2 + 7\text{H}_2\text{O}$.	Found.
Ba	21.99	21.48
H ₂ O	20.22	21.08

II. 0.2912 gram heated at 100—110° lost 0.0214 gram, and gave 0.1285 gram BaSO_4 .

	Calculated for $\text{Ba}(\text{C}_8\text{H}_6\text{NO}_4)_2 + 2\text{H}_2\text{O}$.	Found.
Ba	25.70	25.92
H ₂ O	6.75	7.34

The aqueous solution of the barium salt gives with lead acetate solution a white precipitate, which partially dissolves when boiled and recrystallises on cooling; with silver nitrate solution a white curdy precipitate soluble in ammonia and nitric acid, and finally with ferric chloride a brownish precipitate.

Paramidophenylacetic acid, $\text{C}_8\text{H}_7 \begin{Bmatrix} \text{NH}_2 \\ \text{CH}_2\text{CO}_2\text{H} \end{Bmatrix}$, is prepared by the reduction of the paranitro acid by tin and hydrochloric acid; it crystallises from hot aqueous solutions in white lustrous leaflets, which become brown on exposure to air, and melt at 199—200° with decomposition. The analysis of this acid gave the following numbers:—

0.2357 gram gave 0.5452 gram CO_2 and 0.129 gram water.

			Found.
C ₈	96	63.57	63.08
H ₉	9	5.96	6.06
N	14	9.27	—
O ₂	32	21.20	—
	<hr/>	<hr/>	
	151	100.00	

(2.) *Orthonitrophenylacetic acid*.—The alcoholic mother-liquors from the crystallisation of the paranitro-derivative, when concentrated

yield a body crystallising in white opaque tufts of needles, melting at 112—117°. A similar product is obtained by decomposing the more soluble barium salt with hydrochloric acid. By allowing the solution of this body in methyl or ethyl alcohol to evaporate slowly, large well-formed crystals separate out, which were collected and recrystallised from alcohol. By this means a few grams of these crystals were obtained, melting at 137—138°. When crystallised from hot water, in which they are sparingly soluble, white shining needles separate out at first, and on standing minute crystals appear, having a form similar to the larger ones. Both the needles and the minute crystals melt at 137—138°.

The combustion of the acid crystallised from water gave the following results :—

0.302 gram yielded 0.585 gram CO₂ and 0.1133 gram H₂O.

Calculated for		
$C_6H_5\overset{NO_2}{CH_2}CO_2H.$		Found.
C.	53.03	52.64
H.	3.86	4.13

This acid when oxidised by boiling with a solution of potassium permanganate, yields orthonitrobenzoic acid subliming in white needles, and melting at 141—143°. Moreover, upon reduction it is converted into oxindol, which was recognised by its melting point, 120°, and its reaction with nitrous acid. From these facts I conclude that the second nitro- acid, m. p. 137—138°, is *orthonitrophenylacetic acid*.

For the following description and measurements of the crystals of orthonitrophenylacetic acid, I am indebted to Mr. Baker.

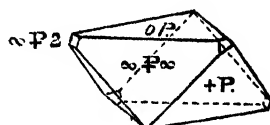
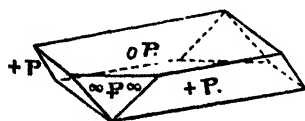
Orthonitrophenylacetic Acid.

Monoclinic. Fig. 1. $0P + P \infty P\infty$; tabular through $0P$.

„ 2. $0P + P \infty P\infty$ in equilibrium, together with $\infty P2$.

$a : b : c = 1.0 : 0.594; L = 97^\circ 17'.$

	Found.	Calculated.
$0P : +P$	$= 51^\circ 45'$	$51^\circ 45'$
$\infty P\infty : +P$	$= 108 \quad 9$	$108 \quad 15$
$0P : \infty P\infty$	$= 97 \quad 17$	$97 \quad 17$
$+P : +P$ (in clino-diagonal)	$= 94 \quad 28$	$94 \quad 28$
$\infty P2 : \infty P2$ (in ortho-diagonal)	$= 81 \quad 16$	$81 \quad 0$

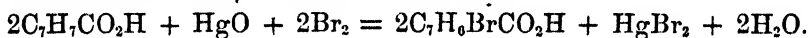


Barium orthonitrophenylacetate crystallises from its aqueous solutions in white lustrous scales, which are more easily soluble in water than the crystals of the corresponding salt of the para-acid. The analysis of this salt shows its formula to be $\text{Ba}(\text{C}_6\text{H}_4\text{NO}_2)_2 + 2\text{H}_2\text{O}$; the water cannot be directly determined as the salt is decomposed at $100\text{--}110^\circ$.

0.495 gram gave 0.2121 gram BaSO_4 , i.e., 25.17 per cent. Ba, whilst $\text{Ba}(\text{C}_6\text{H}_4\text{NO}_2)_2 + 2\text{H}_2\text{O}$ requires 25.70 per cent. Ba.

Aqueous solutions of this barium salt give no immediate precipitate with solution of lead acetate; on standing, however, the lead salt separates out in tufts of fine needles. Silver nitrate and ferric chloride give reactions similar to those with the solutions of the salt of the para-acid.

(3.) *Bromo-derivatives*.—Bromophenylacetic acid was prepared by an application of Barth and Weselky's method for such cases, viz., by treating phenylacetic acid and mercuric oxide suspended in water, with the calculated quantity of bromine in small quantities, at the same time cooling by immersion in water. The reaction which takes place is expressed by the following equation:—



After the completion of the reaction an excess of caustic soda is added, and the filtrate from the mercuric oxide acidified with hydrochloric acid; the bromo-acid separates out as a white crystalline precipitate, and after washing with cold water is crystallised from hot dilute alcohol. The chief portion separates out from this solution as a slightly coloured oil, which on standing solidifies to a crystalline mass; some also crystallises out in tufts of white needles, both portions melting at 76° . The alcoholic mother-liquors on concentration yield an acid having a somewhat higher melting point. This latter portion is converted into the barium salt either by boiling its aqueous solution with barium carbonate or with baryta-water, and in which case the excess of barium is removed by precipitation with carbonic acid. The concentrated aqueous solutions of this salt yield a white crystalline deposit formed of opaque nodular masses; these deposits were crystallised from hot water, and finally decomposed by hydrochloric acid.

Parabromophenylacetic Acid.—The acid thus obtained is dissolved in hot water, from which solution it separates on cooling in long, flat lustrous needles, resembling the crystals of benzoic acid, and melting at $114\text{--}115^\circ$. Its analysis shows it to be a monobromophenylacetic acid, and its melting point is the same as the parabromophenylacetic acid prepared by Loring Jackson, and W. Lowery (*Ber.*, 10, 1210) from parabromobenzyl bromide.

The analysis gave the following results:—

I. 0·256 gram gave 0·4188 gram CO₂ and 0·0786 gram H₂O.

II. 0·2396 gram gave 0·198 gram AgBr and 0·0065 gram Ag.

				Found.	
				I.	II.
C ₈	= 96	44·65		44·60	—
H ₇	= 7	3·25		3·39	—
Br.....	= 80	37·20		—	37·14
O ₄	= 64	17·90		—	—
		<hr/>			
		247	100·00		

Orthobromophenylacetic Acid.—The mother-liquors, containing the more soluble barium salt, which on further evaporation yield no crystalline deposit, were precipitated with a solution of lead acetate, and the white precipitate so formed after washing with cold water was boiled with dilute sulphuric acid. The filtrate from the lead sulphate on cooling yielded crystals of an acid, which, after several crystallisations from hot water, is obtained in the form of long lustrous flat needles, melting at 103—104°, the analysis of which gave the following results:—

I. 0·2104 gram gave 0·3436 gram CO₂ and 0·0584 gram H₂O.

II. 0·257 gram gave 0·2148 gram AgBr and 0·0066 gram Ag.

		Found.	
		I.	II.
C ₈	Calculated. 44·65	44·53	—
H ₇	3·25	3·04	—
Br.....	37·20	—	37·43
O ₂	17·90	—	—
		<hr/>	
		100·00	

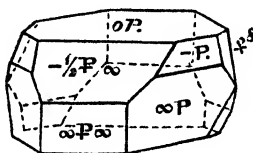
These results, together with the fact that when this acid is oxidised by boiling with a solution of potassium permanganate, orthobromobenzoic acid is formed, melting at 143—144°, prove this acid to be orthobromophenylacetic acid. The orthobromobenzoic acid gave the following results for the bromine determination; 0·1952 gram gave 0·1754 gram AgBr, and 0·0027 gram Ag, giving 39·24 per cent. Br, whereas the formula $C_6H_4\begin{smallmatrix} Br \\ CO_2H \end{smallmatrix}$ requires 39·83 per cent. Br.

Orthobromophenylacetic acid may be obtained in well-formed crystals by the slow evaporation of its solution in glacial acetic acid, for the following description of which I am indebted to Mr. Baker:—

Orthobromophenylacetic Acid.

System monoclinic $\alpha : \bar{b} : c = 1.000 : 0.657 : 1.767$; $L = 99^\circ 44'$
 Forms observed, ∞P . OP . $\infty P\infty$. $\infty\infty$. $-\frac{1}{2}P\infty$. . $-P$.

	Calculated.	Found.
$\infty P : \infty P$ (in ortho-diagonal)	$112^\circ 37'$	$112^\circ 37'$
$OP : \infty P\infty$ (L)	99 44	99 44
$OP : = \frac{1}{2}P \infty$	142 51	142 48
$\infty P : -P$	163 6	163 15
$OP : \infty\infty$	110 40	110 54
$OP : \infty P$	95 23	95 24



From the above experiments bromine in the cold acts on phenylacetic acid in a similar manner to nitric acid, producing para- and ortho-derivatives, in each case the melting point of the "para" is about 12° higher than that of the "ortho." Further, these results show that the parabromophenylacetic acid described by Radziszewski (*loc. cit.*), melting at 76° , is a mixture of the two isomerides. A similar remark may be made with regard to the para- and ortho-nitrophenylacetic acids described by the same chemist, the former melting at 114° and the latter at 98° .

In one of the recent numbers of the *Berliner Berichte* (12, 1764), Maxwell publishes a description of paranitrophenylacetic acid, to which he attributes the melting point 151.5 — 152° , which agrees tolerably well with my determination, as does the description of the methyl- and ethyl-ethers of this acid. The barium salt is described as anhydrous and crystallising in needles, a difference probably due to the method of preparation.

(4.) *Bibromo-derivatives.*—To prepare a bibromo-acid crude bromophenylacetic acid (m. p. 76°) was sealed up in a strong glass vessel with the calculated quantity of bromine, and exposed for several months to the action of sunlight. Thus a brownish liquid was produced, and on opening the vessel quantities of hydrobromic acid were given off. The product after washing several times with water, was converted into the methyl-ether, as all attempts to obtain a crystalline product by crystallisation from alcohol had proved futile, yielding a yellowish viscous mass only. The methyl-ether when distilled under reduced pressure chiefly came over at 220 — 230° ; this

portion was saponified by boiling with caustic potash. The potassium salt decomposed with hydrochloric acid, and an acid obtained which crystallises from water in white shining needles, melting at 114—115°. But a small quantity of this acid was obtained; the bromine determination shows it to be a bibromophenylacetic acid. 0.276 gram gave 0.3521 gram AgBr and 0.0022 gram Ag, which corresponds to 54.78 per cent. Br, whilst $C_6H_4Br_2CH_2CO_2H$ requires 54.42 per cent. Br. Together with this acid other acids are formed, but in quantities insufficient for analysis.

(5.) *Bromonitro-derivatives*.—Short notices of the preparation and separation of two bromonitrophenylacetic acids and the corresponding bromamido-derivatives have already appeared (*Ber.*, 10, 530 and 1637). The following is a more detailed account of these acids, and also of a third isomeride. As in the preparation of these acids I used a bromophenylacetic-acid, melting at 76°, the formation of three bromonitro-acids is not astonishing, as the bromo-acid contained both the para- and ortho-derivatives; it renders doubtful, however, the constitution attributed to the bromonitrophenylacetic acid melting at 167—169°.

Parabromometanitrophenylacetic acid, $C_6H_3 \begin{matrix} NO_2 \\ Br \\ CH_2CO_2H \end{matrix}$, crystallises

from its hot aqueous solutions in small flat greenish-yellow needles, melting at 113—114°. It dissolves in hot water, but is almost insoluble in cold water, and is easily soluble in alcohol and ether.

The analysis of this acid gave the following results:—

- I. 0.3005 gram gave 0.4076 gram CO_2 and 0.0735 gram H_2O .
- II. 0.252 gram gave 0.1736 gram AgBr and 0.0055 gram Ag.
- III. The " NO_2 " determination was made by Limpricht's method, 0.2123 gram gave 0.036768 gram NO_2 .

			Found.		
			I.	II.	III.
C_8	96	36.92	36.97	—	—
H_6	6	2.30	2.66	—	—
NO_2	46	17.68	—	—	17.31
Br	80	30.76	—	30.90	—
O_2	32	13.34	—	—	—
	260	100.00			

This acid when oxidised by potassium bichromate and sulphuric acid yields parabromometanitrobenzoic acid, melting at 197—199°, described by Hübner, Ohly, and Philipp (*Liebig's Annalen*, 143, 248). Its analysis gave the following results:—

- I. 0.2675 gram gave 0.3391 gram CO_2 and 0.05485 gram H_2O .
 II. 0.289 gram gave 0.3635 gram CO_2 and 0.0577 gram H_2O .
 III. 0.3 gram gave 0.221 gram AgBr and 0.0057 gram Ag .

			Found.		
			I.	II.	III.
C_7	=	84	34.14	34.54	34.29
H_4	=	4	1.62	2.23	2.21
N	=	14	5.69	—	—
Br	=	80	32.52	—	32.73
O_4	=	64	26.03	—	—
			246	100.00	

Barium parabromometanitrophenylacetate, $\text{Ba}(\text{C}_6\text{H}_4\text{BrNO}_2)_2 + \text{H}_2\text{O}$, crystallises in yellowish plates or needles united in concentric groups, is soluble in water, but less soluble than the salt of the α -bromitro-acid. The analysis of this salt gave the following results: 0.569 gram heated at 110 — 120° lost 0.154 gram, and gave 0.1969 gram BaSO_4 , corresponding to 2.70 per cent. H_2O and 20.33 per cent. Ba , whilst the formula requires 2.79 per cent. H_2O and 20.35 per cent. Ba .

A dilute solution of the barium salt gives with silver nitrate a white curdy precipitate soluble in nitric acid, with copper acetate a bright blue precipitate, and with lead acetate a white precipitate, which dissolves on boiling.

The methyl ether forms yellowish-white needles usually grouped together, melting at 40 — 41° . Its ethyl ether has only been obtained as an oily liquid.

Parabromometamidophenylacetic acid, $\text{C}_6\text{H}_4 \begin{matrix} \text{NH}_2 \\ \text{Br} \\ \text{CH}_2\text{CO}_2\text{H} \end{matrix}$, obtained by

the reduction of the nitro-acid with tin and hydrochloric acid, crystallises from water in white silky needles, which colour slowly on exposure to the air. It is less soluble in water than the α -bromamido-acid, but is easily soluble in alcohol and chloroform, and sparingly in ether. It melts at 133 — 134° .

Its analysis gave the following result:—0.2156 gram gave 0.3315 gram CO_2 and 0.0714 gram H_2O .

		Calculated for	Found.
		$\text{C}_6\text{H}_4\text{NH}_2\text{BrCH}_2\text{CO}_2\text{H}$.	
C		41.73	41.92
H		3.47	3.66

Its hydrochlorate, $\text{C}_7\text{H}_7\text{BrNCO}_2\text{H.HCl} + \text{H}_2\text{O}$, crystallises in white

needles, united in concentric groups, becoming red on exposure to the air. It is soluble in cold water. The analysis of this salt gave the following results* :—

- I. 0.2636 gram gave 0.1282 gram AgCl and 0.0041 gram Ag.
- II. 0.2208 gram gave 0.275 gram CO₂ and 0.084 gram H₂O.
- III. 0.333 gram gave 0.2168 gram of AgBr.

	Calculated.	Found.		
		I.	II.	III.
C.....	33.72	—	33.96	—
H	3.86	—	4.21	—
Br	28.12	—	—	27.68
Cl	12.47	12.51	—	—

α-Bromonitrophenylacetic acid crystallises from water in yellowish-white, branching needles, melting at 167—169°. It is easily soluble in alcohol and ether, is insoluble in cold water, but soluble in hot water, and less soluble in a mixture of alcohol and water than the isomeric acid already described. The following are the results of its analysis :—

- I. 0.303 gram yielded 0.4106 gram CO₂ and 0.0776 gram H₂O.
- II. 0.5884 gram yielded 0.7955 gram CO₂ and 0.1354 gram H₂O.
- III. 0.5335 gram yielded 0.3861 gram AgBr and 0.004 gram Ag.
- IV. 0.2172 gram by Limpricht's method gives 0.037852 gram "NO₂."

	Calculated.	Found.			
		I.	II.	III.	IV.
C.....	36.92	36.93	36.86	—	—
H.....	2.30	2.83	2.54	—	—
Br	30.76	—	—	31.32	—
NO ₂	17.68	—	—	—	17.42
O.....	13.34	—	—	—	—
<hr/>					
100.00					

The barium salt, Ba(C₆H₄BrNO₂)₂ + 4H₂O, forms yellow transparent needles, united to form concentric groups, is soluble in hot water, less soluble in cold, and more soluble than the salt of the isomeride already described. The following results confirm the above formula :—0.4718 gram heated at 110—115° lost 0.046 gram, and gave

* In I, the chlorine was determined by adding silver nitrate to the aqueous solution of the hydrochlorate; in III, the substance heated with lime, &c., gave a mixture of silver chloride and bromide, and the amount of the latter determined by subtracting the silver chloride given by the chlorine determination.

0.1501 gram BaSO_4 ; or 9.74 per cent. H_2O , and 18.69 per cent. Ba, the formula requiring 9.99 per cent. H_2O and 18.84 per cent. Ba.

The aqueous solutions of the barium give with silver nitrate and lead acetate solution similar reactions to those of the isomeric acid; copper acetate, however, gives a green precipitate.

The methyl-ether forms transparent, slightly yellow, flat, shining needles; it melts at 66–68°. The ethyl-ether forms yellowish needles.

α -Bromamidophenylacetic acid is obtained by reducing the corresponding α -nitro-acid with tin and hydrochloric acid; it crystallises from water in white, brittle needles, which redden on exposure to the air, and melt at 167°, a decomposition taking place at the same time. It is soluble in alcohol and chloroform, but sparingly soluble in ether. Its analysis gave the following results:—

I. 0.2006 gram gave 0.3055 gram CO_2 and 0.0684 gram H_2O .

II. 0.2276 gram gave 0.1692 gram AgBr and 0.0099 gram Ag.

	Calculated.	Found.	
		I.	II.
C	41.73	41.52	—
H	3.47	3.78	—
Br	34.78	—	34.88

The hydrochlorate of α -bromamidophenylacetic acid,



crystallises from water in long white needles, which become red on exposure to the air; it is more soluble in water than the hydrochlorate of the isomeric acid already described. Its analysis gave the following results:—

I. 0.2404 gram gave 0.302 gram CO_2 and 0.0892 gram H_2O .

II. 0.220 gram gave 0.1065 gram AgCl and 0.0034 gram Ag.

III. 0.2029 gram gave 0.1319 gram AgBr .

IV. 0.9059 gram heated in a current of dry air at 90–100°, lost 0.0574 gram.

	Calculated for $\text{C}_6\text{H}_4\text{Br.NH}_2\text{CH}_2\text{CO}_2\text{H.HCl} +$ $\text{H}_2\text{O}.$	Found.			
		I.	II.	III.	IV.
C	33.74	34.23	—	—	—
H	3.86	4.11	—	—	—
Br	28.12	—	—	27.64	—
Cl	12.47	—	12.45	—	—
H_2O	6.32	—	—	—	6.33

The salts of this acid with the alkalis are easily soluble in water;

their solutions give a dark green precipitate with copper acetate of the copper salt.

β-Bromonitrophenylacetic Acid.—Together with the above two bromonitrophenylacetic acids, a third is formed ; it was separated from the yellow crystalline mass obtained by extracting with chloroform the mother-liquors from the nitration of the bromophenylacetic acid. This extract was dissolved in glacial acetic acid, and the solution allowed to evaporate slowly, thus an acid was obtained crystallising in small transparent yellow prisms. It melts at 162°, and when crystallised from hot water it forms long colourless needles, having the same melting point. By reduction with tin and hydrochloric acid, it is converted into a bromamidophenylacetic acid, which crystallises from water in white leaflets, becoming brown on exposure to the air ; it melts at 186°. Its hydrochlorate is less soluble in water than that of either of the above isomerides. But a small quantity of these two acids has been obtained ; the analysis of the bromamido-acid gave the following results :—

- I. 0.213 gram yielded 0.324 gram CO₂ and 0.072 gram H₂O.
- II. 0.2385 gram gave 0.1821 gram AgBr and 0.0061 gram Ag.

	Calculated for C ₆ H ₃ .Br.NH ₂ .CH ₂ CO ₂ H	Found.	
		I.	II.
C.	41.73	41.45	—
H.	3.47	3.75	—
Br.	34.78	—	34.29

From the parabromometamidophenylacetic acid, and the *α*-bromamido-acid, I have attempted to obtain the amidophenylacetic acids by means of the action of sodium amalgam on the aqueous solutions of these acids ; the results of this action are, however, not very satisfactory. Some further clue to the constitution of the above bromonitrophenyl acetic acids I hope to obtain by the preparation of the nitroparamidophenylacetic acids, and from which by means of the diazo reaction to prepare the corresponding bromonitro-derivatives.

IX.—*On the Specific Volume of Water of Crystallisation.*

By T. E. THORPE, F.R.S., and JOHN I. WATTS.

PLAYFAIR and JOULE have pointed out that the volumes of certain highly hydrated salts, *e.g.*, sodium carbonate with 10 mols. of water, and the alkaline arsenates and phosphates with 12 mols., are exactly equal to that of the water, considered as ice, which they respectively contain. The molecules of the salt proper would thus seem to exist in the interstitial spaces of the ice, since they exert no apparent influence on the bulk.

In salts less highly hydrated this law does not hold good. In many of these, as for example, borax with 5 mols. of water, sodium pyrophosphate and normal aluminium sulphate, the volume seems to be made up of the water, considered as ice, together with that of the base as existing in the free state.

Schiff, some years since, showed that the members of certain classes of hydrated salts have practically the same specific volume. Thus all the alums have a specific volume of about 277; double sulphates of the form $M_2.M''(SO_4)_2.6H_2O$ have a common volume of 207; and all the vitriols, that is, the salts of the form $M'SO_4.7H_2O$, whether isomorphous or not, have the specific volume 146.

It is, of course, well known that many salts can unite with water in different proportions to form perfectly definite combinations. Thus, according to various authorities, it is possible to obtain ferrous sulphate combined, at ordinary temperatures, with 1, 2, 3, 4, 5, 6, or 7 mols. of water. Indeed the so-called magnesian sulphates give rise to a larger number of variously hydrated compounds of definite character than any other group of salts.

It appeared to us of interest, especially in view of the investigations of Playfair and Joule, and of Schiff, to determine the precise relation of the specific volume of a salt to its degree of hydration; and in this communication we beg to lay before the Society the results of our observations on such of the variously hydrated sulphates of copper, magnesium, zinc, nickel, cobalt, iron, and manganese as we could obtain in a definite form.

The investigation of this subject was undertaken many years ago by Dr. Playfair, in continuation of the series of researches published by him in conjunction with Dr. Joule, but although considerable progress was made in the work, various circumstances prevented its completion. On learning that one of us was engaged on the question, Dr. Playfair kindly placed the very ample notes of his investigation at

our disposal, and although we have, at his suggestion, gone over the whole of the ground again, much of the experimental matter of the present communication is confirmed by his previous observations. Our investigation was made partly in the laboratory of the Yorkshire College, and partly in that of the Owens College, under Professor Roscoe's supervision.

We give, whenever necessary, the mode of preparation of the various hydrates; the identity of these was in all cases ascertained by analysis, usually by the estimation of the water. The determination of the specific gravity was effected by weighing in benzene, and the final results are the means of several concordant determinations, made by the aid of different bottles. In the case of the anhydrous or other hygroscopic salts the bottles were heated to the proper temperatures after the introduction of the salt, until its weight became constant. In filling the bottles the salt was placed in a small specimen tube, the neck of which was closed by a perforated caoutchouc stopper, through which was inserted the neck of the specific gravity bottle. By shaking the tube when in an inverted position, the salt was made to enter the bottle without undue exposure to air. The weight having been determined, the salt was covered with benzene, the bottle was placed within the receiver of an air-pump, and the exhaustion continued until the benzene boiled. The bottle was then filled up with benzene, and placed in a water-bath having a constant temperature of 15° . The level of the benzene was then adjusted to the mark, and the bottle and its contents again weighed. The benzene had been crystallised, and boiled at about 80° , and was thoroughly dried over sodium. Four determinations of its specific gravity at 15° , compared with water at the same temperature, gave—

I	0.8856
II	0.8860
III	0.8859
IV	0.8857

Mean.... 0.8858

I. *Copper Sulphate.*

1. *Anhydrous Copper Sulphate*, CuSO_4 .—Prepared by heating the pentahydrate to 280° , until it ceased to lose water.

Three determinations of specific gravity gave—

I	3.608
II	3.606
III	3.603

Mean.... 3.606

Other observations on record are—

Filhol	3.530
Joule and Playfair..	3.631
Karsten	3.572
Playfair	3.560

2. *Monohydrated Copper Sulphate*, $\text{CuSO}_4 \cdot \text{H}_2\text{O}$.—Prepared by heating the powdered pentahydrate to 110° , until it ceased to lose weight. A determination of the amount of sulphur gave 18.04 per cent. Theory requires 18.06. The specific gravity bottles were heated to 110° after the introduction of the salt, until the weight was constant.

The determinations of specific gravity gave—

I	3.289
II	3.287
III	3.289
Mean	3.289

Playfair (communicated), 3.296.

3. *Dihydrated Copper Sulphate*, $\text{CuSO}_4 \cdot 2\text{H}_2\text{O}$.—This hydrate, which was first obtained by Playfair, was prepared by pouring a cold saturated solution of copper sulphate into concentrated oil of vitriol, with constant stirring, and washing the precipitated salt with absolute alcohol, until free from acid. A determination of water gave 18.24 per cent. Theory, 18.45.

Two determinations of specific gravity gave—

I	2.952
II	2.954
Mean	2.953

Playfair found that a similar preparation had a specific gravity of 2.891. He also obtained the dihydrate by boiling the finely powdered pentahydrate with absolute alcohol. A determination of water gave 18.26 per cent; its specific gravity was 2.878 (mean of two determinations).

4. *Trihydrated Copper Sulphate*, $\text{CuSO}_4 \cdot 3\text{H}_2\text{O}$.—This salt, which appears not to have been made before, was obtained by us by pouring a cold saturated solution of copper sulphate into an equal volume of sulphuric acid of sp. gr. 1.7. The precipitate was washed with small quantities of absolute alcohol, until free from uncombined sulphuric acid.

Analysis: 1.3952 gram gave 0.349 gram water = 25.01 per cent. Calculated, 25.34.

0.5913 gram gave 0.6568 gram BaSO_4 = 15.25 S per cent. Calculated, 15.02.

Two determinations of specific gravity gave—

I	2·663
II	2·663

All attempts to prepare the tetrahydrate were unsuccessful. A salt of the composition $\text{CuSO}_4 \cdot 3\frac{1}{2}\text{H}_2\text{O}$, *heptahydrated copper sulphate*, was, however, obtained by placing the finely powdered pentahydrate over concentrated oil of vitriol until it ceased to lose weight even after prolonged exposure.

An estimation of copper by standard potassium cyanide gave 28·60 per cent. Theory requires 28·40.

Two determinations of specific gravity gave—

I	2·645
II	2·645
Mean	2·645

A second series of observations on another preparation gave—

I	2·650
II	2·652
Mean	2·651

This salt also appears not to have been obtained before.

5. *Pentahydrated Copper Sulphate*, $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$.—Prepared by repeatedly crystallising the commercial salt. 1·6523 gram gave 0·5939 gram water = 35·96 per cent. Theory, 36·13.

Two determinations of specific gravity gave—

I	2·282
II	2·281
Mean	2·282

The specific gravity of a second preparation, which was found to give off 36·35 per cent. of water, was—

I	2·284
II	2·288
Mean	2·286

Other observations on record are—

Joule and Playfair	2·278
"	"	2·290
Kopp	2·274
Filhol	2·286
Stolba	2·279

Summary of Results of Observations on Hydrated Copper Sulphates.

Hydrate	0	1	2	3	3½	5
Molecular weight.	159·1	177·1	195·1	213·1	222·1	249·1
Specific vol. according to—						
T. and W.	44·1	{ 55·4 53·8 }	66·1	80·0	{ 84·0 83·8 }	{ 109·1 109·0 }
Playfair	44·7	53·7	67·8	—	—	—
Joule and Playfair	43·8	—	—	—	—	{ 109·3 108·7 }
Karsten	44·5	—	—	—	—	—
Filhol	44·9	—	—	—	—	109·0
Kopp	—	—	—	—	—	109·5
Stolba	—	—	—	—	—	109·3
Mean	44·4	54·3	67·0	80·0	83·9	109·1

II. *Magnesium Sulphate.*

1. *Anhydrous Magnesium Sulphate*, MgSO_4 .—Prepared by heating the heptahydrate to 280° , until it ceased to lose weight.

The determinations of specific gravity gave—

I	2·708
II	2·710
Mean	2·709

Other observers have found—

Filhol	2·628
Pape	2·675
Joule and Playfair	2·706

2. *Monohydrated Magnesium Sulphate*, $\text{MgSO}_4 \cdot \text{H}_2\text{O}$.—Obtained by heating the heptahydrate to 130 — 140° , until it ceased to lose weight.

Two determinations of specific gravity gave—

I	2·442
II	2·447
Mean	2·445

Playfair found that the monohydrate prepared in the same manner, and which lost 13·24 per cent. water (calculated 13·04) had a specific gravity of 2·478 (mean of two observations). *Kieserite* ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), according to Bischof, has a specific gravity of 2·517.

3. *Dihydrated Magnesium Sulphate*, $\text{MgSO}_4 \cdot 2\text{H}_2\text{O}$.—Obtained by boiling the finely powdered heptahydrate with absolute alcohol.

2·0175 grams lost 0·4735 gram water = 23·40 per cent. Calculated, 23·08.

Two determinations of specific gravity gave—

I	2·374
II	2·372
	<hr/>
Mean....	2·373

Playfair, who also obtained this salt in the manner described above, and likewise by heating the heptahydrate to 100°, found its specific gravity to be 2·279.

4. *Pentahydrated Magnesium Sulphate*, $\text{MgSO}_4 \cdot 5\text{H}_2\text{O}$.—This salt was obtained by Playfair by drying the heptahydrate over strong sulphuric acid in air, until it ceased to lose weight. It contained 43·05 per cent. of water. Theory requires 42·8. Its specific gravity (mean of two determinations) was 1·869.

5. *Hexhydrated Magnesium Sulphate*, $\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$.—Prepared by crystallising a solution of the ordinary salt at above 40°.

2·7717 gram lost 1·309 gram water = 47·2 per cent. Theory, 47·37.

The determinations of specific gravity gave—

I	1·734
II	1·734
	<hr/>
Mean....	1·734

Playfair, who prepared the salt in the same manner, found its specific gravity to be 1·751.

6. *Heptahydrated Magnesium Sulphate*, $\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$.—Prepared by recrystallising Epsom salts. 1·415 gram lost on heating 0·7255 gram water = 51·2 per cent. Calculated, 51·2.

A determination of specific gravity gave 1·676.

A second preparation containing 51·23 per cent. of water gave the following numbers :—

I	1·678
II	1·678
	<hr/>
Mean....	1·678

Other observations on record are—

Hassenfratz	1·660
Kopp	1·674
Joule and Playfair	1·683
Schiff	1·685
Buignet	1·675

Summary of Results of Observations on Hydrated Magnesium Sulphate.

Hydrate	0	1	2	5	6	7
Molecular weight	120	138	156	210	228	246

Specific volume according to—

T. and W.	44.3	56.4	65.7	—	131.5	{ 146.8 146.6
Filhol	45.6	—	—	—	—	—
Pape	44.9	—	—	—	—	—
Joule and Playfair..	44.4	—	—	—	—	146.2
Playfair	—	55.7	68.4	112.4	130.2	—
Bischof	—	54.8	—	—	—	—
Kopp	—	—	—	—	—	146.9
Schiff	—	—	—	—	—	146.0
Buignet	—	—	—	—	—	146.9
Mean.....	44.8	55.6	67.0	112.4	130.8	146.6

III. *Zinc Sulphate.*

1. *Anhydrous Zinc Sulphate*, ZnSO_4 .—Obtained by heating the heptahydrate to 280—300°, until it ceased to lose water.

Determinations of specific gravity—

I	3.629
II	3.627
Mean....	3.628

A second preparation gave the following numbers:—

I	3.621
II	3.617
Mean....	3.619

Other observations on record are:—

Filhol	3.400
Playfair	3.413
Joule and Playfair.....	3.681
Pape	3.435

2. *Monohydrated Zinc Sulphate*, $\text{ZnSO}_4 \cdot \text{H}_2\text{O}$.—Prepared by heating the heptahydrate to 100—110°, until it ceased to lose weight.

1.2433 gram lost 0.1275 gram water = 10.26 per cent.

1.3623 " 0.1395 " = 10.24 "

Theory = 10.04 per cent.

Two determinations of specific gravity gave—

I	3.283
II	3.278
Mean....	3.280

A second preparation afforded the following numbers:—

I	3.287
II	3.291
Mean....	3.289

A determination of specific gravity made by Playfair on a salt containing 10.08 per cent. of water gave 3.259.

3. *Dihydrated Zinc Sulphate*, $\text{ZnSO}_4 \cdot 2\text{H}_2\text{O}$.—Obtained by pouring a cold saturated solution of zinc sulphate into strong sulphuric acid, and washing the precipitate with absolute alcohol until free from uncombined acid.

1.371 gram salt gave 0.2495 gram water = 18.1 per cent.

Theory = 18.2 „

Two determinations of specific gravity gave—

I	2.958
II	2.957
Mean....	2.958

4. *Pentahydrated Zinc Sulphate*, $\text{ZnSO}_4 \cdot 5\text{H}_2\text{O}$.—This salt was obtained by boiling the finely powdered heptahydrate with alcohol of sp. gr. 0.825 (Playfair); 7.174 grains lost 2.549 grains water, or 35.5 per cent. Theory, 36.0.

Two determinations of specific gravity gave—

I	2.197
II	2.205
III	2.217
Mean....	2.206

5. *Hexhydrated Zinc Sulphate*, $\text{ZnSO}_4 \cdot 6\text{H}_2\text{O}$.—Obtained by crystallising a solution of zinc sulphate at about 40°.

Determinations of specific gravity—

I	2.071
II	2.073
Mean....	2.072

Playfair also obtained this salt by crystallising a solution at about 30°.

10·35 grains gave 4·175 grains water, or 40·30 per cent. Theory requires 40·29.

Its specific gravity was found to be 2·056.

6. *Heptahydrated Zinc Sulphate*, $\text{ZnSO}_4 \cdot 7\text{H}_2\text{O}$. — Ordinary white vitriol, after repeated crystallisation, contained the following amounts of water:—

1·6963 gram	gave	0·7441 gram	water or	43·87 per cent.
1·5160	„	0·6648	„	43·85 „
Theory 43·87 per cent.				

Its specific gravity was found to be—

I	1·963
II	1·963

A second sample gave the following numbers:—

I	1·965
II	1·965

Other observations on record are:—

Joule and Playfair..	1·931 (mean of 4 observations).
Schiff	1·953
Buignet	1·957
Stolba	1·9534
Holker	1·976

Summary of Results of Observations on Hydrated Zinc Sulphates.

Hydrate.....	0	1	2	5	6	7
Molecular weight....	161	179	197	251	269	287

Specific volume according to—

T. and W.....	{ 44·5 44·3 }	{ 54·3 54·6 }	66·6	—	129·6	{ 146·2 146·0 }
Filhol	47·2	—	—	—	—	—
Playfair	47·1	55·3	—	113·7	130·8	148·6
Joule and Playfair.	43·7	—	—	—	—	148·5
Pape	46·8	—	—	—	—	—
Schiff	—	—	—	—	—	146·9
Buignet	—	—	—	—	—	146·6
Stolba	—	—	—	—	—	146·9
Holker	—	—	—	—	—	145·3
Mean.....	45·6	54·7	66·6	113·7	130·2	146·8

IV. *Nickel Sulphate.*

1. *Anhydrous Nickel Sulphate*, NiSO_4 . — Prepared by heating a weighed quantity of the heptahydrated salt at 250° , until it ceased to lose weight.

2·964 grams lost 1·330 grams H_2O . Calculated loss = 1·33 grams.

Two determinations of specific gravity gave:—

I	3·419
II	3·417
		<hr/>
Mean...		3·418

Playfair obtained 3·526.

2. *Monohydrated Nickel Sulphate*, $\text{NiSO}_4 \cdot \text{H}_2\text{O}$. — Prepared by heating the heptahydrate at 100° , until its weight was constant.

0·3585 gram lost 0·0360 gram H_2O = 10·03 per cent. Theory, 10·40.

3. *Hexhydrated Nickel Sulphate*, $\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$. — Prepared by crystallising a solution of nickel sulphate at a temperature above 40° .

0·4682 gram lost on heating 0·191 gram = 40·8 per cent. Theory, 41·2.

A determination of specific gravity gave 2·031.

Topsoë obtained values varying from 2·042 to 2·074.

4. *Heptahydrated Nickel Sulphate*, $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$. — So-called pure nickel sulphate of commerce was freed from cobalt by treatment with chlorine, adding barium carbonate in excess, filtering, precipitating the nickel in the filtrate with potash, and, after well washing, dissolving the oxide in sulphuric acid and recrystallising.

2·964 gram lost 1·33 gram on heating = 44·9 per cent. Theory, 44·9.

Two determinations of specific gravity gave:—

I	1·949
II	1·948
		<hr/>
Mean...		1·949

A determination on a second preparation gave 1·945.

Schiff observed 1·931.

Summary of Results of Observations on Hydrated Nickel Sulphate.

Hydrate.....	0	1	6	7
Molecular weight.....	154.7	172.7	262.7	280.7

Specific volume according to—

T. and W.	45.2	56.6	—	{ 144.1 144.3
Playfair	43.9	56.4	129.3	—
Topsoë	—	—	128.6	—
Schiff	—	—	—	145.4
Mean.....	44.6	56.5	129.0	144.6

V. Cobalt Sulphate.

1. *Anhydrous Cobalt Sulphate*, CoSO_4 .—Obtained by drying the heptahydrate at 250° . A determination of specific gravity gave 3.472. Playfair obtained 3.444.

2. *Monohydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot \text{H}_2\text{O}$.—Prepared by heating the heptahydrate at 100° until it ceased to lose weight. Its specific gravity was found to be 3.125.

3. *Dihydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot 2\text{H}_2\text{O}$.—Prepared by boiling the finely powdered heptahydrate with absolute alcohol.

0.229 gram lost 0.0435 gram water = 18.9 per cent.; calculated 18.9. The specific gravity was 2.668. Playfair also obtained the salt in the same manner, and found the specific gravity to be 2.712.

4. *Tetrahydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot 4\text{H}_2\text{O}$.—Obtained by exposing the finely powdered heptahydrate over oil of vitriol, until its weight was constant. Sp. gr. 2.327.

5. *Pentahydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot 5\text{H}_2\text{O}$.—This hydrate was obtained by Playfair by drying the heptahydrated salt over sulphuric acid.

3.475 grams gave 1.290 gram water = 37.1 per cent. Calculated, 36.7. A determination of specific gravity gave 2.134.

6. *Hexahydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot 6\text{H}_2\text{O}$.—Prepared by crystallising a solution of cobalt sulphate at about 25° .

0.5400 gram lost 0.2190 gram H_2O = 40.6. Theory 41.2. The specific gravity was found to be 2.019.

7. *Heptahydrated Cobalt Sulphate*, $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$.—Prepared by recrystallising pure cobalt sulphate. The salt was freed from nickel by treatment with chlorine and barium carbonate, solution in acid, reprecipitation with potash, and re-solution in sulphuric acid.

A determination of specific gravity gave 1.918. Schiff observed 1.924.

Summary of Results of Observations on Cobalt Sulphate.

Hydrate	0	1	2	4	5	6	7
Molecular weight.	154·7	172·7	190·7	226·7	244·7	262·7	280·7

Specific volume according to—

T. and W.	44·5	55·2	71·5	97·4	—	130·1	146·4
Playfair	44·9	—	70·3	—	114·6	—	—
Schiff	—	—	—	—	—	—	145·5
Mean....	44·7	55·2	70·9	97·4	114·6	130·1	146·0

VI. *Manganous Sulphate.*

1. *Anhydrous Manganous Sulphate*, MnSO_4 .—Obtained by heating the pentahydrate to 280° until it ceased to lose weight. Its specific gravity was found to be 3·282. Playfair observed 3·386.

2. *Monohydrated Manganous Sulphate*, $\text{MnSO}_4 \cdot \text{H}_2\text{O}$.—Prepared by drying the pentahydrate at 100° until no further loss of weight was observed.

1·1315 gram lost 0·1250 gram H_2O = 11·04 per cent. Theory 10·74. A determination of specific gravity gave 2·845. Playfair observed 3·210.

3. *Dihydrated Manganous Sulphate*, $\text{MnSO}_4 \cdot 2\text{H}_2\text{O}$.—Obtained by boiling the finely powdered pentahydrate with absolute alcohol. This hydrate may also be prepared by pouring a saturated solution of the pentahydrate into oil of vitriol.

1·183 gram lost 0·2275 gram water = 19·20 per cent. Theory 19·35.

Two determinations of specific gravity gave :—

I	2·526
II	2·525
Mean....	2·526

4. *Trihydrated Manganous Sulphate*, $\text{MnSO}_4 \cdot 3\text{H}_2\text{O}$.—Obtained by Playfair by evaporating a solution of the sulphate at a boiling heat until a pellicle formed on the surface, removing this and drying it rapidly between hot filter-paper.

5·875 grains gave 1·535 grains H_2O = 26·1 per cent. Theory, 26·2. Sp. gr. 2·356.

5. *Tetrahydrated Manganous Sulphate*, $\text{MnSO}_4 \cdot 4\text{H}_2\text{O}$.—This hydrate, according to Topsoë, has a specific gravity of 2·261.

6. *Pentahydrated Manganous Sulphate*, $\text{MnSO}_4 \cdot 5\text{H}_2\text{O}$.—Obtained by repeatedly crystallising the ordinary sulphate. Two concordant deter-

minations of specific gravity gave 2.103. Kopp obtained 2.095 and 2.087.

Summary of Results of Observations on Manganous Sulphates.

Hydrate	0	1	2	3	4	5
Molecular weight....	150	168	186	204	222	240
Specific volume according to—						
T. and W.	45.7	59.1	73.6	—	—	114.1
Playfair.....	44.3	52.3	—	86.6	—	—
Topsoë	—	—	—	—	98.2	—
Kopp.....	—	—	—	—	—	{ 114.5 114.8
Mean....	45.0	55.7	73.6	86.6	98.2	114.4

VII. *Ferrous Sulphate.*

1. *Anhydrous Ferrous Sulphate*, FeSO_4 .—Obtained by heating the powdered heptahydrate in a current of hydrogen. Analysis showed that it was anhydrous. Its specific gravity was 3.346. Playfair observed 3.48.

2. *Monohydrated Ferrous Sulphate*, $\text{FeSO}_4 \cdot \text{H}_2\text{O}$.—Prepared by heating the powdered heptahydrate in a current of hydrogen at 120° . An estimation of iron by potassium permanganate solution gave 32.6 per cent. Theory, 32.9. Sp. gr. 2.994. Playfair found 3.047.

3. *Dihydrated Ferrous Sulphate*, $\text{FeSO}_4 \cdot 2\text{H}_2\text{O}$.—Obtained by boiling the heptahydrate with successive quantities of absolute alcohol. Sp. gr. 2.773.

4. *Tetrahydrated Ferrous Sulphate*, $\text{FeSO}_4 \cdot 4\text{H}_2\text{O}$.—Obtained by exposing the finely powdered heptahydrate over oil of vitriol in an atmosphere of carbon dioxide until it ceased to lose weight. An estimation of iron by standard potassium permanganate solution gave 25.3 per cent. Calculated, 25.0. Sp. gr. 2.227.

5. *Heptahydrated Ferrous Sulphate*, $\text{FeSO}_4 \cdot 7\text{H}_2\text{O}$.—It has been thought unnecessary to add to the determinations of the specific gravity of this salt already on record.

Joule and Playfair.....	1.889
Filhol	1.904
Schiff	1.884
Buignet	1.902

Summary of Results of Observations on Ferrous Sulphates.

Hydrate	0	1	2	4	7
Molecular weight.	152	170	188	224	278

Specific volume according to—

T. and W.	45·4	56·7	67·7	100·5	—
Playfair	43·6	55·7	—	—	—
Joule and Playfair	—	—	—	—	147·2
Filhol	—	—	—	—	146·0
Schiff	—	—	—	—	147·5
Buignet	—	—	—	—	146·1
Mean	44·5	56·2	67·7	100·5	146·7

On comparing the foregoing observations, it is evident that the anhydrous sulphates of copper, magnesium, zinc, nickel, cobalt, manganese, and iron, have identical specific volumes; or since we may define specific volume as the volume in cubic centimetres occupied by the equivalent of the salt in grams, it follows that equivalent quantities of these different sulphates occupy the same bulk in space. A like conclusion as regards certain of these anhydrous sulphates has already been drawn by Playfair and Joule.

A further consideration of the numbers warrants us, we believe, in supposing that this conclusion may be extended to the various hydrates of these salts. The evidence on which this assumption is grounded is contained in the following table, which is merely a synopsis of the experimental results detailed in the foregoing pages:—

Hydrate.	0	1	2	3	4	5	6	7
Copper sulphate	44·4	54·3	67·0	80·0	—	109·1	—	—
Magnesium sulphate . . .	44·8	55·6	67·0	—	—	112·4	130·8	146·6
Zinc sulphate	45·6	54·7	66·6	—	—	113·7	130·2	146·8
Nickel sulphate	44·6	56·5	—	—	—	—	129·0	144·6
Cobalt sulphate	44·7	55·2	70·9	—	97·4	114·6	130·1	146·0
Manganous sulphate . . .	45·0	55·7	73·6	86·6	98·2	114·4	—	—
Ferrous sulphate	44·5	56·2	67·7	—	100·5	—	—	146·7
Mean of means	44·8	55·5	68·8	83·3	98·7	112·9	130·0	146·1

Some of these numbers are not so precise as we could wish: it would have been more satisfactory, for example, to have obtained a larger number of observations on the trihydrates. But these intermediate hydrates are obtained with great difficulty owing in great part to the indefinite character of the methods of preparation; indeed, by

far the greater portion of the time occupied in what has proved to be a very tedious research, was spent in attempts, in many cases futile, to procure them in a state of purity. An examination of our experimental data will make it clear that the disparities between the values obtained for the different members of each series are almost entirely due to accidental variations in the degree of hydration of the salts, and not to errors in the determinations of the specific gravities; errors of this kind, such as are likely to occur, would exercise only a comparatively small influence on the result. That the disparities are actually accidental would seem to be proved by the fact that no regularity or symptom of order can be discovered in the mode of the variation. We think, therefore, we are justified in concluding that what Playfair and Joule have shown to be true of certain of the anhydrous sulphates of the form $M''SO_4$, and what Schiff has shown to hold good in the case of the hydrated sulphates of the form $M''SO_4 \cdot 7H_2O$ —and their results are confirmed by our own independent observations—is equally applicable to the case of the intermediate hydrates. The final mean, then, of each series will afford us an approximation to the true specific volume of the particular hydrate, and enable us, therefore, to trace the influence of the varying degree of hydration on the bulk of the salt.

The first and main conclusion we draw from our observations is that, in the case of the so-called magnesian sulphates, the volume occupied by the several molecules of water varies with the degree of hydration. The first molecule of water, the constitutional water, or "water of halhydration" of Graham, occupies considerably less bulk than the remaining molecules; its mean relative value is 10·7. Each additional molecule appears to occupy a gradually increasing volume. The difference between the monohydrate and dihydrate is 13·3; between the dihydrate and trihydrate it is 14·5; between the trihydrate and tetrahydrate it is 15·4. There is a break in the continuity of the rate between the tetrahydrate and pentahydrate, due to the low value found for copper sulphate. The difference between the hexhydrate and heptahydrate is 16·2. We give these numbers merely as first approximations, since a far larger number of observations made upon hydrates of definite composition will be required to fix the exact values. We would point out, however, that our main conclusion is in harmony with experience. The general fact that the different molecules of water in a hydrated salt are held with varying degrees of tenacity, as shown by the difference in the intensity of heat needed to expel them, is of course well known. Now, as has already been pointed out by Müller, chemical combination is generally attended by contraction, and the stability of the resulting compound corresponds with, if it is not dependent on, the diminution of bulk. It would be a problem of con-

siderable interest, in the light of these results, to determine the different quantities of heat evolved in the combination of successive molecules of water with these anhydrous sulphates. Graham, nearly forty years since, made the beginning of such a research. From comparative experiments made with the anhydrous sulphates of manganese, copper, zinc, and magnesium, and the monohydrates of these salts, Graham found that far more heat was developed in the act of combination of the first molecule—that in which the greatest contraction occurs—than is evolved in the combination of any of the remaining molecules; the amount in the case of the first molecule was from a fourth to a third of that needed for the complete hydration of the salt.

These observations have been greatly extended by Favre and Valson (*Compt. rend.*, **73**, 1144; **74**, 1016, 1065; **75**, 798, 925, 1000, 1066, 1071), who have determined the amount of heat produced or abstracted by the solution of sulphates of various degrees of hydration in water. The observations were made on a number of the sulphates mentioned in the foregoing pages, on certain double sulphates and on the alums. The results, so far as they are applicable to the salts under consideration, are as follows :*

	Heat-units.
CuSO_4	8149
$\text{CuSO}_4 \cdot \text{HO}$	4734
$\text{CuSO}_4 \cdot 5\text{HO}$	— 1216
MgSO_4	10152
$\text{MgSO}_4 \cdot \text{HO}$	5493
$\text{MgSO}_4 \cdot 7\text{HO}$	— 1860
ZnSO_4	9289
$\text{ZnSO}_4 \cdot \text{HO}$	4812
$\text{ZnSO}_4 \cdot 7\text{HO}$	— 2074
$\text{NiSO}_4 \cdot 7\text{HO}$	— 1944
$\text{CoSO}_4 \cdot 7\text{HO}$	— 1680
MnSO_4	7085
$\text{MnSO}_4 \cdot \text{HO}$	4216
$\text{MnSO}_4 \cdot 5\text{HO}$	235
$\text{FeSO}_4 \cdot 7\text{HO}$	— 2182

These numbers, which express the amount of heat evolved by the solution of 1 equiv. of the salt in grams in 1 litre of water, are not exactly comparable with those of Graham, but they serve to confirm the general conclusion that the heat due to the combination of the first molecule of water is much greater than that evolved in the combination of the succeeding molecules.

* O = 8, S = 16.

X.—*Note on the Formation of Ozone during the Slow Oxidation of Phosphorus.*

By HERBERT McLEOD.

WHEN preparing my lecture on ozone during the recent term, it seemed advisable to ascertain if this body is really produced during the slow oxidation of phosphorus in moist air, as some doubts have lately been thrown on its formation by this process. The experiments extended to an unforeseen length, and it may be well to give a short account of them, although it is necessary to apologise for bringing merely qualitative experiments under the notice of the Society.

The active substance formed during the slow oxidation of phosphorus is probably either ozone or peroxide of hydrogen; the direction the experiments took, therefore, was to decide which of these bodies was present in the air in which phosphorus was undergoing oxidation.

It is well known that hydroxyl is readily destroyed by alkalis, by a solution of chromic acid, and by a solution of an alkaline permanganate, while ozone is unaffected by a solution of sodic carbonate, and by chromic acid, and appears to be only slightly attacked by the alkaline permanganate.

Ozonised oxygen prepared by passing dried oxygen through a Siemens tube of the form employed by Sir Benjamin Brodie (*Phil. Trans.*, 1872, 162, 438), was passed through a U-tube 9½ inches long filled with glass and containing in succession sodium carbonate solution (previously saturated with carbonic anhydride to remove any possible trace of free alkali), a mixture of potassium dichromate and sulphuric acid, and potassium permanganate previously saturated with carbonic anhydride. In all these cases the ozone passed through even when the U-tube was surrounded with boiling water.

Hydroxyl, on the contrary, is readily decomposed by a solution of sodic carbonate, especially at the temperature of boiling water, a mixture of hydroxyl and sodium carbonate effervescing powerfully when a test-tube containing it is plunged in boiling water; it immediately transforms chromic into perchromic acid at the common temperature, and when it is mixed with potassium permanganate, oxygen is rapidly evolved.

Corresponding experiments were made with the air in which phosphorus was slowly oxidising. A wide cylinder was covered by a loosely fitting perforated glass plate, through which a glass tube, reaching nearly to the bottom of the cylinder, was passed. A stick of phosphorus lay horizontally at the bottom of the cylinder, and was partly

immersed in water. The air was drawn through the **U**-tube previously mentioned, and then into a flask containing a solution of potassic iodide and starch: in all cases the solution became blue, both when the **U**-tube containing the reagents was cold and heated to 100°.

It was possible that the gas did not come intimately in contact with the reagents in the **U**-tube filled with broken glass; another tube, 12½ inches long, was therefore constructed and filled with very small pieces of pumice-stone tightly packed. The pumice-stone was saturated with solution of sodic carbonate; in this case also the active gas passed.

It seemed desirable that the effect of heat should be tried on the gas. For this purpose an apparatus was constructed consisting of a large **U**-tube containing pumice-stone and sulphuric acid, a narrow **U**-tube which could be heated in a test-tube, a weighed tube containing pumice-stone and sulphuric acid, and a flask with a solution of potassium iodide and starch acidified by sulphuric acid. Some of the joints were made, as suggested by Brodie, by slipping a wide tube over the ends of the separate parts of the apparatus and filling the annular space with melted paraffin; those on each side of the tube to be weighed consisted of wide tubes fitted with corks through which the narrow tubes passed, and in order to prevent to some extent the action of the corks on the gas, a tube a very little larger than the narrow ones was slipped over the ends. Quantities of the gas from the phosphorus cylinder, varying between 1 litre and 5 litres, were drawn slowly (at the rate of about a litre an hour) through the apparatus. In some cases the narrow **U**-tube was left at the ordinary temperature, sometimes plunged in boiling water, and sometimes in melted paraffin at temperatures of 150° and 200°. The **U**-tube was weighed before and after each experiment; and the blue solution obtained by the action of the gas on the potassium iodide and starch was at the end of each experiment decolorised by a decinormal solution of sodium thiosulphate. There was very little regularity in the results, and it appeared as if the increase of weight of the second sulphuric acid tube was due to the escape of some of the phosphorous acid through the first tube, and with the formation of water. That some of the phosphorous acid did pass through the first tube was shown by a slight white ring which formed inside the narrow **U**-tube at the level of the melted paraffin. The maximum increase of weight in twenty-four experiments was .0035 gram; this took place in an experiment in which the small **U**-tube was cold, and in this case the quantity of solution of sodium thiosulphate employed to decolorise the solution was 3.65 c.c. As the formation of active gas by the phosphorus is by no means regular, it would be impossible to compare the results with one another; but four consecutive experiments although not made on the same day, gave the following numbers:—

Gas aspirated.	Temperature of U-tube.	Increase of weight of sulphuric acid tube.	Quantity of thiosulphate solution required to decolorise blue liquid.
4600 c.c.	cold	·0026 gram	2·55 c.c.
2760 „	100°	·0008 „	1·9 „
4600 „	150°	·0026 „	3·2 „
2760 „	200°	·0006 „	1·8 „

Now as 1 c.c. of the solution of the thiosulphate corresponds to ·017 gram of hydroxyl, which on decomposition by heat would form ·009 gram of water, and as we may reasonably assume that, at 200°, at least one-half of any hydroxyl that might be present would be decomposed, we should in the last experiment expect an increase of about ·016 gram in the sulphuric acid tube instead of only ·0006.

Hydroxyl is known to combine with acids, and it may therefore be expected that strong sulphuric acid would absorb it: to see if the gas from phosphorus was rendered inactive by contact with sulphuric acid, a bulb of about 200 c.c. capacity was blown on a tube, and some of the air from the phosphorus cylinder drawn into it. One end of the tube was now sealed, and the other dipped into sulphuric acid, and the bulb warmed to expel some of the gas; on cooling the acid entered the bulb, which was then turned round so as to moisten the sides. The bulb was left in this condition for four days, being occasionally shaken so as to renew the surface of the acid. The point was then cut off and the gas drawn through potassic iodide and starch, which was immediately rendered blue.

It may be thought that hydroxyl and ozone are simultaneously produced during the oxidation of phosphorus; but this is hardly possible, for the bodies mutually decompose one another under certain conditions. To examine the action of these substances on one another, some commercial peroxide of hydrogen was introduced into a cylinder of ozonised oxygen, and, to my surprise, the gas in the cylinder affected ozone paper even after prolonged agitation. If, however, the small quantity of acid mixed with the hydroxyl is neutralised with sodium carbonate, or the liquid made very slightly alkaline, the ozone is destroyed in a few minutes. During the oxidation of phosphorus an acid is of course formed, and this may prevent the mutual action of the ozone on the peroxide, although it seems hardly probable.

The above experiments seem to show that the gas obtained during the slow oxidation of phosphorus possesses the properties of ozone, and not the properties of the only known peroxide of hydrogen; whether any other product is formed remains to be proved.

XI.—*On the Analysis of Organic Bodies containing Nitrogen, &c.*

By W. H. PERKIN, F.R.S.

IN the ordinary process for the analysis of nitrogenous organic bodies the use of freshly reduced copper has been found to possess many drawbacks. In the first place the copper is very hygroscopic, and it also appears to occlude hydrogen, so that the hydrogen determinations are always more or less too high, this error being serious when small quantities of substance are under examination. Oxygen also cannot be used freely at the commencement of the combustion. These difficulties have been overcome to a great extent by the use of metallic silver instead of copper, but silver has the great disadvantage of requiring a very high temperature to make it act efficiently, a disadvantage which is very serious if the combustion-tube used be not very infusible.

The method about to be referred to was to some extent the outcome of experiments made some years since in an attempt to obtain not only the determination of the carbon and hydrogen by combustion, but also that of the halogens. To obtain this result it was necessary to burn the substance thoroughly in oxygen, avoiding the use of cupric oxide, lead chromate, &c., the products of combustion being then passed over a weighed quantity of heated metallic silver.

The arrangement actually used consisted of a combustion-tube with about twelve inches of the central part filled with crumpled platinum foil. In the front of this a weighed roll of thick silver foil, supported on platinum rings at each end, was placed for the absorption of the halogens as they came forward as hydrogen-acids or in the free state. The substance was burnt in a boat at the back part of the tube, oxygen being supplied both *before* as well as behind it.

But as most of the substances I wished to burn contained nitrogen, the difficulty arose as to how to get rid of the nitrous fumes produced. It was evident that no process of reduction could be used, as an excess of oxygen was always present. To get over this difficulty, it was thought that perhaps some process of oxidation and absorption might be used, and recourse was had to the process used in the combustion of sulphur compounds, viz., the introduction of a tube filled with

plumbic peroxide between the arrangements for absorbing the water produced and the carbonic anhydride. This succeeded so far as the carbon determinations were concerned, but as the water was absorbed in sulphuric acid, this acid likewise dissolved a large quantity of the nitrous fumes, and the hydrogen determinations were in consequence usually high. Nevertheless, some tolerably good results were obtained, as, for example, in the analysis of the aniline platinum salt, which yielded carbon, hydrogen, chlorine, and platinum determinations in one combustion. The process, however, was found uncertain, and the halogen determinations varied with different specimens of combustion tubing, some being acted on to a considerable extent, especially when substances containing bromine were burnt in them.

Since making these experiments, I have often thought it desirable to do away with the use of copper in the combustion of nitrogenous bodies, especially when I have had to burn small quantities of substance; and, therefore, fresh attempts were made in this direction.

As the use of plumbic peroxide between the sulphuric acid bulb or tube and the potash-bulbs was efficient only so far as the carbon was concerned, experiments were made by placing plumbic peroxide in the combustion-tube itself, in the position usually occupied by the reduced copper. This part of the tube was made to project outside the combustion furnace, so that the plumbic peroxide employed and the plumbic nitrate formed during the combustion might not be decomposed by overheating. But to prevent moisture being retained by its contents, either during the preliminary drying or in the actual combustion, it was made to rest in a thick copper trough, which was heated to a suitable temperature by means of a Bunsen burner. This method, though a great improvement, was not altogether satisfactory, as the plumbic peroxide had to be heated with care, it was difficult to ensure its being thoroughly dry, and thus the hydrogen determinations were uncertain. It is quite likely this difficulty might be overcome by using some more trustworthy method of heating the plumbic peroxide, but the introduction of further precautions was not desirable, as I was seeking for a simple process.

On further consideration it appeared that the thing wanted was some stable oxidising agent containing a metal which would also yield a stable nitrite or nitrate, and it appeared that potassic chromate fulfilled these conditions. Experiments were therefore made with it first to see if it would absorb nitrous fumes diluted with air, and it was found to do so both when cold and when heated, provided of course the stream of gas was not too rapid. It also did not appear to com-

bine with carbonic anhydride, but as this was a most important thing to prove, especially as it is stated in "Watts's Dictionary" that this salt is "decomposed by carbonic acid, yielding the acid potassic chromate," a combustion of sugar was made in the ordinary way, but with a layer of about 6 inches of potassic chromate in the front part of the tube, which was kept at a scarcely dull red heat. The result obtained was exceptionally good, proving that nothing had to be feared on this score. (The statement quoted above is probably intended to refer to solutions of the chromate, and not to the dry salt.)

Combustions of uric acid were then made in the same manner as the above one with sugar, this substance being selected on account of the large percentage of nitrogen it contains, and also because when burnt with cupric oxide and oxygen it yields large quantities of nitrous fumes. Azobenzene was also used. These experiments gave satisfactory results, no oxides of nitrogen appearing.

So far as I have worked with it, this process appears to be both good and simple, and capable of giving much better hydrogen determinations than when copper is used. I have, therefore, thought it best to bring it before the Society in its present state, and without waiting until it is further elaborated. I will, therefore, only add a few remarks, which I hope may be useful to any who may wish to adopt it.

With reference to the potassic chromate, it is of course essential that it should be free from any excess of alkali. The presence of bichromate in small quantities, however, could not be harmful, but bichromate alone does not appear to work so well as chromate. The chromate should be roughly powdered or, better, granulated by evaporating its solution to dryness with constant stirring; it does not then decrepitate so violently when heated. I am now trying pumice-stone coarsely powdered which has been saturated with a solution of potassium chromate and then dried, and it promises to work better than the pure salt.

The length of the combustion-tube to be filled with it will necessarily vary with the amount and nature of the substance to be burnt. For uric acid I have generally filled a length of about 6 or 7 inches, but with most bodies I believe about four or five inches sufficient.

The temperature to which the chromate should be heated appears to be of some importance. This salt is not at all easily fusible, the temperature employed in a combustion furnace not being sufficient for

this purpose, so that during the drying operation it can be heated just in the same manner as the copper oxide. This, however, is unnecessary, as the salt is an anhydrous one, and easily dried, and a high temperature is only a needless expenditure of gas, and it is possible that after the chromate has been used several times, and will then contain nitrate or nitrite, a high temperature might be injurious, as these salts become alkaline from decomposition, though most probably chromate would simply be regenerated. I have not experienced any difficulty in this direction. The temperature used during combustion is worth attention, although I have obtained good results both when using a dull red or only a gentle heat.

The following results will illustrate the importance of this, especially when a short length of potassic chromate is used:—

Three combustions of uric acid were made, to see how short a length of chromate would be sufficient to absorb all the nitrous fumes; about four inches were used, and about 0.15 gram of substance burnt. In the first two experiments the chromate was kept at a very dull red heat; in both of these a small quantity of red fumes passed from the combustion-tube, but not enough to vitiate the results, the hydrogen being a little increased, about 0.2 per cent. The third combustion was made with the chromate only very gently heated at first, but raised to about a dull red at the close of the operation. Not a trace of red fumes appeared, and the results were good.

The cause of this difference I think is not difficult to explain. During the combustion the red fumes are associated with steam, and if the temperature be high, this steam would have but little influence, if any, on the potassic chromate, but if low, it would more or less influence the surfaces of the crystals, and thus the nitrous fumes would be constantly having fresh chromate to act upon.

I cannot say how many times the chromate can be used with safety, but evidently a considerable number of times.

Potassic chromate absorbs not only nitrous fumes, but sulphurous acid, so that it would be useful in the combustion of organic bodies containing sulphur, or both sulphur and nitrogen. It will not absorb iodine vapours perfectly, if at all, but it would be probably useful in the combustion of bodies containing chlorine or bromine. I have not, however, as yet made any experiments in this direction.

XII.—The Melting and Boiling Points of certain Inorganic Substances.

By T. CARNELLEY, D.Sc., Professor of Chemistry, Firth College, Sheffield, and W. CARLETON-WILLIAMS, Assistant Lecturer on Chemistry, Owens College.

THE melting points of the following substances were determined by the specific heat method, which has been previously described by one of us (this Journal, 1876, 1, 489, and 1878. Trans., 273).

Substance.	M. p.	Mean.	Remarks.
	°	°	
Tellurium .. {	438 } 445 } 458 }	455 {	A pure sample obtained from Trommsdorf.
Tellurium {	479 } 452 }	452 {	
			This specimen was purified by Mr. L. Wills (this Journal, 1879, Trans., 704) by distillation in hydrogen, &c., and was used by him in determining the atomic weight of the element.
TeCl ₂ {	201 } 213 } 213 }	209 {	Measured by a thermometer.
TeCl ₄ {	— } — }	224 (corr.) about 280° {	
TeBr ₄ {	371 } 379 } 389 }	380 {	Prepared by dissolving cuprous oxide in hydrobromic acid. A determination of the copper in this specimen agreed with the calculated result.
Cu ₂ Br ₂ {	494 } 502 } 515 }	504 {	
Rb ₂ CO ₃ {	830 } 836 } 845 }	837 {	Prepared by ignition of the acid tartrate.
CsCl {	626 } 632 } 634 }	631 {	From pure caesium alum.
NaBrO ₃ {	379 } 383 } 597 }	381 {	
KClO ₄ {	600 } 618 } 624 }	610 {	
KIO ₃ {	559 } 561 } 570 }	560 {	This salt undergoes partial decomposition, iodine being evolved.
KIO ₄ {	586 } 590 }	582 {	This salt decrepitates at 389° and melts at 582°.
BiI ₃ {	— }	below 439° {	Decomposes with evolution of iodine; the residue melts at 462°. In sealed capillary tubes the salt melts below 439°.

The following melting points were determined by suddenly plunging sealed capillary tubes containing the salts into a zinc chloride bath at different temperatures, and observing whether fusion took place:—

BeCl_2 , 585—617° } Prepared by passing chlorine or bromine over a
 BeBr_2 , 585—617 } mixture of charcoal and beryllia.
 Fe_2Cl_6 , 306—307 Begins to sublime below 100°.
 Cr_2Cl_6 decomposes, with liberation of chlorine, but does not melt.

The boiling points of several metallic salts were determined by the method which has been previously described by us in this Journal (1878, Trans., 281, and 1879, Trans., 563). In the following table Column I contains the name of the substance, II, the salts used in measuring the boiling point, the symbol + being used to indicate that the salt melts, and — to show that it has not fused. III gives the melting points of these salts, and IV the boiling point of the substance.

I.	II.	III.	IV.	Remarks.
Cuprous chloride	$\left\{ \begin{array}{l} + \text{Na}_2\text{SO}_4 \\ + \text{Ag} \\ - \text{Cu} \end{array} \right.$	$\left\{ \begin{array}{l} 861 \\ 954 \\ 1032 \end{array} \right.$	(954—1032)	From Trommsdorf.
Cuprous bromide	$\left\{ \begin{array}{l} + \text{Na}_2\text{SO}_4 \\ - \text{Ag} \\ - \text{Cu} \end{array} \right.$	$\left\{ \begin{array}{l} 861 \\ 954 \\ 1032 \end{array} \right.$	(861—954)	$\left\{ \begin{array}{l} \text{Prepared by passing SO}_2 \\ \text{through a solution of} \\ \text{CuSO}_4 \text{ and KBr; also by} \\ \text{dissolving cuprous oxide} \\ \text{in hydrobromic acid.} \\ \text{Analysis gave 44.20 per} \\ \text{cent. Cu calculated 44.25.} \end{array} \right.$
Cuprous iodide	$\left\{ \begin{array}{l} + \text{KCl} \\ + \text{MoO}_3 \\ - \text{NaCl} \\ - \text{Na}_2\text{CO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 734 \\ 759 \\ 772 \\ 814 \end{array} \right.$	(759—772)	$\left\{ \begin{array}{l} \text{Prepared by precipitating} \\ \text{CuSO}_4 \text{ with KI, in pre-} \\ \text{sence of sulphurous acid.} \\ \text{Decomposes with evolu-} \\ \text{tion of iodine.} \end{array} \right.$
Cadmium bromide	$\left\{ \begin{array}{l} + \text{Pb}(\text{PO}_3)_2 \\ + \text{Pb}_2\text{P}_2\text{O}_7 \\ - \text{BaBr}_2 \\ - \text{Na}_2\text{CO}_3 \end{array} \right.$	$\left\{ \begin{array}{l} 800 \\ 806 \\ 812 \\ 814 \end{array} \right.$	(806—812)	$\left\{ \begin{array}{l} \text{Prepared by the action of} \\ \text{bromine on cadmium in} \\ \text{the presence of alcohol.} \end{array} \right.$
Cadmium iodide	$\left\{ \begin{array}{l} + \text{Li}_2\text{CO}_3 \\ + \text{NaBr} \\ - \text{CaCl}_2 \\ - \text{KCl} \end{array} \right.$	$\left\{ \begin{array}{l} 695 \\ 708 \\ 719 \\ 734 \end{array} \right.$	(708—719)	$\left\{ \begin{array}{l} \text{Prepared by dissolving me-} \\ \text{tallic cadmium in hydi-} \\ \text{iodic acid.} \end{array} \right.$
Lead iodide	$\left\{ \begin{array}{l} \text{Na}_2\text{CO}_3 \\ \text{Na}_2\text{SO}_4 \\ - \text{Ag} \end{array} \right.$	$\left\{ \begin{array}{l} 814 \\ 861 \\ 954 \end{array} \right.$	(861—954)	$\left\{ \begin{array}{l} \text{Prepared by dissolving pure} \\ \text{lead in hydriodic acid.} \\ \text{Slowly decomposes on} \\ \text{boiling with liberation of} \\ \text{iodine.} \end{array} \right.$
Tellurium bromide	—	—	339	Measured by a thermometer.

The melting points of silver and copper have recently been redeter-

mined by Violle (*Compt. rend.*, Oct. 27th, 1879), and we have made use of his numbers in the preceding experiments.

The adoption of these numbers involves an alteration in our last paper (*Chem. Soc. Trans.*, 1879), viz., the substitution of 861—954° for 861—1000° as the temperature at which lead chloride, cadmium chloride, and metallic sodium boil.

The melting points of four of the above compounds were calculated by the method recently described by one of us (*Proc. Roy. Soc.*, 1879, No. 197). The calculated numbers agree fairly well with the experimental results, as is seen from the following data:—

	Calculated.	Observed.
CsCl	below 959°	904°
Cu ₂ Br ₂ . . .	782	777
BeCl ₂	820—870	858—890
BeBr ₂	802—820	858—890

In our last communication (*Chem. Soc. Trans.*, 1879, 565) we drew attention to the fact that our determinations of the temperature of the boiling points of antimony, tin, bismuth, and lead differed considerably from the boiling points of these metals as calculated by Wiebe's method (*Ber.*, 12, 788), and we now find that the observed boiling points of cadmium iodide and lead iodide by no means agree with the temperature calculated by means of Wiebe's formula.

	Calculated.	Observed.
CdI ₂	597°	708—719°
PbI ₂	547	861—954

In conclusion we may point out a curious fact in connection with the melting and boiling points of the mercuric and cuprous halogen compounds, viz., that in the mercuric compounds the melting point sinks and the boiling point rises with an increased molecular weight, whilst in the cuprous compounds the reverse is the case; the melting point rises and the boiling point falls.

	Chlorides.	Bromides.	Iodides.
Mercuric . . { m. p. . .	287°	244°	241°
{ b. p. . .	303	319	349
Cuprous . . { m. p. . .	434	504	601
{ b. p. . .	954	861	760

XIII.—*On the Reaction between Sodium Thiosulphate and Iodine.
Estimation of Manganese Oxides and Potassium Bichromate.*

By SPENCER UMFREVILLE PICKERING, B.A., Brackenbury Scholar of Balliol College, Oxford.

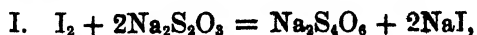
IN estimating the amount of manganese dioxide contained in various mixtures of the oxides of manganese, as described in a former paper, (this Journal, 1879), a modification of Bunsen's volumetric method was employed, which, although it had not been previously noticed by other chemists, appeared sufficiently obvious to require no special mention.

Instead of boiling the oxides with hydrochloric acid and collecting the evolved chlorine in a solution of potassium iodide (F. Mohr, *Lehrb. d. Chem. Analyt. Titrimethode*, 4 aufl., 278), or digesting them at 100° in a stoppered bottle containing hydrochloric acid and the iodide (*ibid.*, 281), the sample to be analysed was transferred to a beaker containing a large excess of this latter solution, a small quantity of acid added, and the liberated iodine determined by directly running into this mixture a standard solution of sodium thiosulphate. The oxides, if in a state of fine powder, and especially if recently precipitated, were found to be dissolved readily by very dilute acid in the presence of the iodide.

On comparing analyses made in this manner with those made according to Bunsen's directions, it was found that the former nearly always yielded slightly higher results than the latter: this fact led to the following investigation of the various circumstances which influence the reactions involved.

PART I.—*Reactions between Sodium Thiosulphate and Iodine.*

§ 1. *Amount of Sulphate formed.*—It is well known that in the reaction between iodine and sodium thiosulphate, if the liquid be warm, then, besides the action—



another action also takes place, resulting in the formation of a sulphate according to the equation—



Notwithstanding the statements of Rose (*ibid.*, 270) and others, a qualitative test sufficed to show that some sulphate is formed, even at

ordinary temperatures, and although the amount was not large, it was sufficient to admit of its being determined quantitatively.*

The sodium thiosulphate, which contained $\cdot 013704$ gram $\text{Na}_2\text{S}_2\text{O}_3$ per c.c., contained also some sulphate, and this had to be determined by blank experiments. The following numbers were obtained:—

100 c.c. of the sodium thiosulphate yielded.....	$\left\{ \begin{array}{l} \text{A } \cdot 000229 \\ \text{B } \cdot 000233 \\ \text{C } \cdot 000235 \end{array} \right\}$	$\cdot 000232$ gram BaSO_4 per c.c.
100 c.c. of the sodium thiosulphate added to an extremely slight excess of iodine at 20°C yielded.....	$\left\{ \begin{array}{l} \text{A } \cdot 000336 \\ \text{B } \cdot 000341 \\ \text{C } \cdot 000339 \\ \text{D } \cdot 000344 \end{array} \right\}$	$\cdot 000340$ gram BaSO_4 per c.c.

hence an amount of sulphate corresponding to $\cdot 000108$ gram BaSO_4 is formed in the oxidation of $\cdot 013704$ gram $\text{Na}_2\text{S}_2\text{O}_3$ by iodine at 20°C ., or the number of molecules of iodine reacting according to the equations I and II is 1 and 46.6 respectively.†

§ II. *Effect of Temperature.*—In order to obtain some idea as to the effect of temperature on these two reactions, a series of experiments was performed, in each of which 10 c.c. of an iodine solution (containing $\cdot 020672$ gram of iodine per c.c.) kept in a bath at a definite temperature was titrated by the thiosulphate. The results thus obtained are given in Table I.

Blank experiments were first performed to ascertain whether any appreciable loss of iodine took place from volatilisation during the titration of the warm solution. The iodine solution was heated to about 50°C . (the highest temperature employed in any of the experiments) in a stoppered bottle; some water was then run into it from the burette, the stopper replaced, and the solution cooled. It was then titrated; no loss of iodine has taken place during these operations.

Before the addition of the last drop of the thiosulphate solution the liquid was in every case allowed to attain the temperature of the room.

* Owing to this formation of sulphate the neutral solution of thiosulphate becomes distinctly acid after the addition of the iodine, as would be inferred from equation II.

In order that the thiosulphate used in these experiments should be as pure as possible it was recrystallised three or four times, and before the addition of the iodine to its solution both these reagents were mixed separately with a few drops of barium chloride solution and allowed to stand for 24 hours, so that any trace of sulphate present in them might be detected and eliminated.

That the sulphate formed at ordinary temperatures in the reaction under discussion could not have been entirely, or even principally, due to any sulphite present in the thiosulphate, is shown by the fact that its amount is considerably reduced by a reduction of temperature.

† Molecule for molecule, potassium thiosulphate was found on oxidation with iodine to yield nearly the same amount of sulphate as the sodium salt.

TABLE I.—*Showing the Influence of Temperature on the Actions.*

Iodine solution taken.	Temperature.	Thiosulphate required.	Weight of iodine reacting to form tetrathionate.	Weight of iodine reacting to form sulphate.
10 c.c.	—	2·352 c.c.*	0	100
"	52° C.	18·18 } 18·17 c.c.	96·10	3·90
"	"	18·16 }		
"	50° "	18·207 c.c.*	96·32	3·68
"	43 "	18·32 c.c.	97·00	3·00
"	40 "	18·35 c.c.*	97·17	2·83
"	31 "	18·43 } 18·42 c.c.	97·63	2·37
"	"	18·41 }		
"	30° "	18·426 c.c.*	97·65	2·35
"	20 "	18·47 c.c. (see Table VI)	97·90	2·10
"	15 "	18·485 c.c.*	98·03	1·97
"	10 "	18·497 c.c.*	98·06	1·94
"	0 "	18·51 }		
"	"	18·52 } 18·51 c.c.	98·16	1·84
"	"	18·50 }		
"	—	18·816 c.c.*	100	0

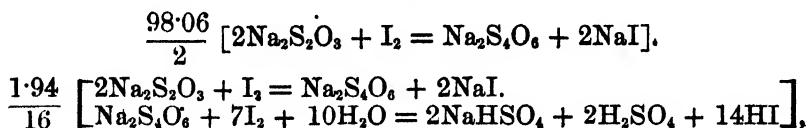
The above experiments are essentially a reproduction of those made by Wright in 1870† (*Chem. News*, 21, 103). He, however, does not appear to have recognised the formation of any sulphate at temperatures below 28° C. (the iodine not being in excess), and its formation above this temperature he attributes to the oxidising action of the iodine on the tetrathionate formed in the first stages of the reaction, and not to the direct oxidation of the thiosulphate according to equation II, page 128. The following considerations, however, appear to render such a view untenable:—

(1.) If the sulphate were formed by the oxidation of the tetrathionate, then, when the iodine is added to the thiosulphate, we should expect that less sulphate would be formed than when the thiosulphate is added to the iodine, for in the latter case some tetrathionate is in the presence of excess of iodine throughout the reaction, whereas in the former case no excess of iodine is present at any time. The experiments given in Table VI, however, show that the reaction is the same whether the iodine be added to the thiosulphate or the thiosulphate to the iodine.

* Interpolated.

† Wright did not make any direct determination of the sulphate formed: his experiments consisted chiefly in ascertaining the relative amounts of iodine required for the oxidation of a given quantity of sodium thiosulphate between the temperatures of 16° and 92° C.

(2.) In the case of the sulphate being formed by the oxidation of the tetrathionate, the results of the experiment at 10° C. (for instance) given in Table I would be represented by the following equations:—



from which, taking the titres of the various solutions and the quantities used as given above, we find that during the ten minutes allowed for the reaction .00352 gram of iodine has been used in oxidising some of the sodium tetrathionate formed into sulphate, the total quantity of tetrathionate formed being 0.216 gram.

In order to ascertain whether the oxidation of sodium tetrathionate does in reality take place at this rate, several portions of a pure sample of this salt, weighing .216 gram each, were dissolved in water, and 10 c.c. of the iodine solution added to each.* The residual iodine was subsequently determined after various intervals of time had elapsed, the temperature being kept constant at 10° C.

The following were the results obtained:—

	c.c.		gram.			
After 10 mins.	0.01	of iodine, or	.000207	I per 10 mins.	had disappeared.	
„ 19 $\frac{5}{8}$ hrs.	0.38	„ „	.000066	„ „	„ „	
„ 24 $\frac{1}{8}$ „	0.40	„ „	.000057	„ „	„ „	
„ 46 $\frac{1}{8}$ „	0.70	„ „	.000052	„ „	„ „	
„ 69 „	1.05	„ „	.0000525	„ „	„ „	

The amount of oxidation is thus seen to diminish considerably as the action proceeds,† but taking the first experiment, which gives by far the highest rate (possibly due in part to the difficulty of measuring such small differences as .01 c.c.), we find that this rate is less than one-twelfth of what it should be if the sulphate were formed (in the reaction of iodine on thiosulphate) by the oxidation of the tetrathionate, and not by the direct oxidation of the thiosulphate.

§ III. *Effect of Dilution.*—The experiments given in Table II were performed in order to ascertain whether the amount of water present had any influence on the relative proportions in which the two above-

* This is, of course, a great exaggeration of the conditions existing in the experiment in Table I, for here we have both the maximum amount of tetrathionate, and also the maximum amount of iodine present at the same time, whereas in the ordinary determination when either of these substances is at a maximum the other is at a minimum.

† This diminution in rate is not due to the presence of the sodium sulphate formed, for on adding excess of this substance the rate of oxidation was not found to be appreciably altered.

mentioned reactions (page 128) take place. Dilution is here seen to cause a small increase in the amount of sulphate formed, less of the thiosulphate being required according as the quantity of water present is greater. Its effect, however, is very slight, for in order to make the experiments strictly comparable, a small correction must be applied, since it was found that a quantity of iodine ($\cdot 000042$ gram) equivalent to $\cdot 004$ c.c. of the thiosulphate was requisite for every 50 c.c. of solution to give a visible coloration with starch.

TABLE II.—*Showing the Effect of Dilution.*

Iodine solution taken.	Water added.	Thiosulphate solution required.	Thiosulphate corrected for final reaction.
10 c.c.	None	18·47 c.c. (see Table VI)	18·47 c.c.
"	50 c.c.	18·47	18·467 c.c.
"	"	18·47	
"	"	18·46	
"	100 c.c.	18·46	18·457 "
"	"	18·45	
"	"	18·46	
"	150 c.c.	18·45	18·447 "
"	"	18·42	
"	"	18·44	
"	"	18·45	18·435 "
"	"	18·43	
"	"	18·42	
"	200 c.c.	18·44	18·435 "
"	"	18·43	
"	250 c.c.	18·42	
"	"	18·43	18·42 "
"	300 c.c.	18·41	
"	"	18·42	

§ IV. *Amount of Potassium Iodide present.*—The experiments given in Table III show that the presence of an excess of potassium iodide over that necessary for the solution of the iodine, has no effect on the quantity of thiosulphate used.

TABLE III.—*Showing the effect of Excess of Potassium Iodide.*

Iodine solution taken.	Excess of KI added.	Thiosulphate solution required.
10 c.c.	None (see Table VI)	18·47 c.c.
"	1 gram	18·46 "
"	"	18·47 "
"	2 grams	18·47 "
"	"	18·47 "
"	3 "	18·46 "
"	"	18·47 "

§ V. *Influence of Time.*—A series of experiments were next performed with a view of ascertaining whether in a dilute solution of iodine in potassium iodide the amount of the former diminished appreciably on being kept for various lengths of time. The solutions to be titrated were placed in stoppered bottles inverted in a vessel containing starch water, so that any leakage might be detected. Some of them were kept in the dark, others in diffused daylight. In both cases, however, no sensible diminution in the amount of free iodine present was found to have taken place within four days,* that time being the extreme limit allowed in any of the experiments. The results are given in Table IV.

TABLE IV.—*Showing the Influence of Time.*

Iodine solution added.	Water added.	Interval between dilution and titration.	Thiosulphate required.
10 c.c.	150 c.c.	None	18·45 to 18·42 c.c. (see Table II)
"	"	$\frac{1}{2}$ hr.	18·44 c.c.
"	"	"	18·45 "
"	"	1 hr.	18·45 "
"	"	"	18·43 "
"	"	2 " hrs.	18·43 "
"	"	"	18·44 "
"	"	$3\frac{1}{2}$ hrs.	18·42 "
"	"	5 "	18·42 "
"	"	6 "	18·45 "
"	"	7 "	18·45 "
"	"	18 $\frac{1}{2}$ "	18·42 "
"	"	"	18·44 "
"	"	24 "	18·43 "
"	"	30 "	18·43 "
"	"	48 "	18·44 "
"	"	96 "	18·42 "

§ VI. *Influence of Hydrochloric Acid.*—In order to ascertain whether the reactions under consideration were influenced by the presence of hydrochloric acid, the amount of iodine liberated by treating potassium iodide with the latter substance had previously to be determined.

* It is scarcely necessary to mention that precautions were taken for detecting any change in the titre of the standard solutions; the iodine and thiosulphate were compared together, and the latter compared with a standard solution of potassium bichromate at least once in every 24 hours. In order to facilitate comparison of results in the tables given, the actual amount of thiosulphate employed is reduced to what it would have been had the solutions remained unaltered throughout.

The addition of a little sodium hydrate greatly increases the stability of the thiosulphate (Harcourt and Eason, *Phil. Trans.*, 5, 156, p. 205).

5 c.c. of the acid employed (density 1.156 at 20° C. = 31.6 per cent. HCl) when added to 0.5 gram potassium iodide dissolved in 45 c.c. of water were found—

To liberate at once.....	·00123 gram I	{ (mean of many expts.)
To have liberated after 24 hours	·00515 "	
" " another 24 hours	·00515 "	
" " "	·00504 "	
" " "	·00526 "	
" " "	·00493 "	
" " "	·00515 "	
" " "	·00515 "	

Mean ·00512 gram I per 24 hours.

To have liberated after 96 hrs. ·01725 gram I = ·00431 gram I per 24 hours.

With the quantities of potassium iodide and water above mentioned the iodide liberated at once was found to be proportional to the hydrochloric acid added when the quantity of this latter was varied between 1 and 15 c.c., though with larger quantities than 5 c.c. the final action becomes rather uncertain.

The results obtained by titrating definite quantities of iodine solution in presence of hydrochloric acid are given in Table V, and show that the acid has no influence on the relative proportions in which the reactions I and II, page 128, take place. In these, and other similar experiments, the thiosulphate was run into the iodine solution as soon as it had been mixed with the acid and cooled down to 20° C., 10 minutes being allowed in every case for the reaction to complete itself.

TABLE V.—*Showing the Influence of Hydrochloric Acid present.*

Iodine solution taken.	HCl added.	Thiosulphate required.	Correction for I liberated by HCl.	Thiosulphate required, corrected.
10 c.c.	None	18.47 c.c. (see Table VI)	None	18.47 c.c.
"	1 c.c.	18.50 c.c.	·02 c.c. thiosulphate	18.48 "
"	3 "	18.58 "	·065 c.c. "	18.465 "
"	" "	18.53 "	·065 "	18.465 "
"	4 "	18.56 "	·09 "	18.47 "
"	5 "	18.57 "	·11 "	18.46 "
"	" "	18.58 "	·11 "	18.47 "
"	" "	18.58 "	·11 "	18.47 "
"	10 "	18.69 "	·22 "	18.47 "
"	" "	18.68 "	·22 "	18.46 "

§ VII. *Iodine added to excess of Thiosulphate.*—The results given in Table VI show that no difference in the amount of sulphate formed is made by adding the iodine solution to excess of thiosulphate, and subsequently determining that excess by means of a standard solution of iodine instead of adding the thiosulphate to the iodine.*

TABLE VI.

Thiosulphate added to Iodine.		Iodine added to excess of Thiosulphate.	
Iodine solution taken.	Thiosulphate required.	Iodine solution taken.	Thiosulphate required.
10 c.c.	18·47 c.c.	10 c.c.	18·46 c.c.
"	18·47 "	"	18·47 "
"	18·47 "	"	18·47 "
"	18·47 "	"	18·46 "
"	18·46 "	"	18·47 "
"	18·47 "	"	18·47 "
"		"	18·47 "

The case, however, is different if hydrochloric acid is present. The results obtained under these circumstances are given in Table VII,

TABLE VII.—*Iodine and Acid added to Thiosulphate.*

Iodine solution taken.	HCl added.	Thiosulphate required.	Correction for I liberated by HCl.	Corrected thiosulphate.	Iodine indicated by the thiosulphate used.
10 c.c. ..	None	18·47 c.c. (see Table VI)	None	18·47 c.c.	100·00
" ..	1 c.c.	18·48	{ ·02 c.c. thio-sulphate }	18·45 "	99·89
" ..	" "	18·46 } 18·47 c.c.		"	"
" ..	2 "	18·48 c.c.	{ ·045 c.c. thio-sulphate }	18·435 "	99·81
" ..	3 "	18·45	{ ·065 c.c. thio-sulphate }	18·41 "	99·67
" ..	" "	18·50 } 18·475 c.c.		"	"
" ..	4 "	18·46	{ ·09 c.c. thio-sulphate }	18·38 "	99·51
" ..	" "	18·48 } 18·47 c.c.		"	"
" ..	" "	18·47	{ ·11 c.c. thio-sulphate }	18·325 "	99·22
" ..	5 "	18·43		"	"
" ..	" "	18·40 } 18·435 c.c.		"	"
" ..	" "	18·47		"	"
" ..	" "	18·44			

* Finkener probably ascertained this fact, see Rose, *Handb. d. Anal. Chem.*, 6 Aufl., von Finkener, 2, 937.

and show that an increase in the amount of sulphate formed is occasioned by the presence of the acid, the greater being that increase according as the quantity of acid present is greater. In these experiments, since the acid liquid could not be added to excess of the thio-sulphate without causing its decomposition, the iodine solution, mixed with the acid, was added to nearly the necessary volume of thio-sulphate (18.3 c.c.) and the additional quantity required run into this mixture. It is also to be noticed that the individual experiments in this series are less concordant among themselves than in any other series.

PART II.—*Estimation of Manganese Oxides and Potassium Bichromate.*

§ I. *Valuation of Manganese Oxides.*—In valuing the oxides of manganese according to Bunsen's method three different forms of apparatus were employed:—(1) The oxide was boiled in a small flask fitted with a thistle funnel, the chlorine evolved being absorbed in three other flasks containing potassium iodide solutions; the flasks were fitted with india-rubber stoppers, and a current of air was drawn through the whole apparatus during the experiment. (2) The oxide was boiled with the acid in a small retort, the neck of which was bent down and fitted by means of an india-rubber plug into the first of three U-tubes containing potassium iodide solution; no current of air was employed. With this, and also with the first apparatus, no chlorine ever passed beyond the second absorption vessel. (3) The ebullition was performed in a small retort, as in the second case, the neck of which passed into a larger inverted retort containing potassium iodide solution.

With the first two arrangements identical results were obtained; with the third one, however, a small loss of chlorine was found to take place, owing to there being but one vessel for its absorption. In most cases apparatus (1) was employed as being found the most convenient of the three.

Traces of chlorine were found to be retained by the acid liquid even after prolonged boiling, and these were estimated by pouring some solution of potassium iodide into the flask before disconnecting it from the absorption vessels, and determining the iodine liberated in this flask separately from that liberated in the others.* A given number of minutes was allowed for the ebullition, cooling, and determination of the iodine, the amount of iodine liberated by boiling a given quantity of hydrochloric acid alone being determined in each special case by blank experiments.

* It was ascertained that neither the acid nor the oxides employed contained any traces of iron.

The results thus obtained with a sample of pure artificial manganese oxide are given in Table I, together with the numbers obtained with the modification of Bunsen's method, described on page 128 (due correction being also made in this case for the iodine liberated by the acid, 5 c.c. of which were employed in each determination). Provided the acid used in Bunsen's method be not diluted, both methods yield practically identical results; a small quantity of water, however, caused an appreciable diminution in the amount of chlorine liberated, and this diminution becomes greater as the amount of water added is increased, but in a decreasing ratio.

From 0.2 to 0.3 gram of the oxide was used in each analysis, this quantity requiring 20–30 c.c. of the thiosulphate.

TABLE I.—*Analyses of Manganese Oxide.*

Method employed.	Percentage of available oxygen found.	Relative quantity of available oxygen found.
Modification of Bunsen's method	6.938	100.00
" "	6.922	
" "	6.940	
" "	6.923	
" "	6.936	
Bunsen's method; using 10 c.c. HCl and no water	6.922	99.97
" " "	6.938	
" " "	6.934	
" " "	6.918	
" " "	6.938	
Ditto; using 10 c.c. HCl, and 5 c.c. water	6.900*	99.54
Ditto; using 10 c.c. HCl, and 10 c.c. water	6.877	99.24
" " " " "	6.881	
Ditto; using 10 c.c. HCl, and 15 c.c. water	6.864*	99.01
Ditto; using 10 c.c. HCl, and 20 c.c. water	6.872	98.904
" " "	6.862	
" " "	6.840	
" " "	6.850	
Ditto; using 10 c.c. HCl, and 30 c.c. water	6.824	98.56
" " "	6.841	
" " "	6.831	
Ditto; using 10 c.c. HCl, and 50 c.c. water	6.794	98.30
" " "	6.801	
" " "	6.832	
" " "	6.829	

* Interpolated by means of a curve.

§ II. *Analyses of Potassium Bichromate.*—A series of experiments, similar to those just described, were performed, substituting potassium bichromate for the manganese oxide. The results are given in Table II, and are found to agree with those in Table I; they show, however, that in the case of potassium bichromate the discrepancy between results obtained by the two methods is greater than with manganese oxide, and thus, even when the acid employed in Bunsen's method is undiluted, a notable deficiency of chlorine is observed.

TABLE II.—*Analyses of Potassium Bichromate.*

Method employed.	Potassium bichromate taken.	Thiosulphate required.	Relative quantity of thiosulphate used.
Modification of Bunsen's method	·1522 gram	35·05	100·00
" "	"	35·04	
" "	"	35·04	
" "	"	35·04	
" "	"	35·05	
" "	"	35·04	
" "	"	35·04	
Bunsen's method; using 10 c.c. HCl, and no water	·1522 gram	34·84	99·40
" "	"	34·83	
" "	"	34·83	
" "	"	34·83	
" "	"	34·84	99·17
" "	"	34·84	
" "	"	34·75	
" "	"	34·76	
Ditto; using 10 c.c. HCl, and 3 c.c. water	"	34·75	98·984
" "	"	34·76	
" "	"	34·76	
" "	"	34·75	
Ditto; using 10 c.c. HCl, and 5 c.c. water	"	34·69*	98·90
" "	"	34·66	
" "	"	34·66	
" "	"	34·66	
Ditto; using 10 c.c. HCl, and 10 c.c. water	"	34·625*	98·70
" "	"	34·595*	
" "	"	34·59	
" "	"	34·60	
" "	"	34·58	

§ III. *Loss of Chlorine.*—In order to ascertain whether the well-known formation of hydrochloric acid in chlorine water at ordinary

* Interpolated by means of a curve.

temperatures was sufficiently increased at 100° C. to account for the low results obtained by Bunsen's method, some chlorine water was heated for various times at different temperatures, either in stoppered bottles or in sealed tubes, and the numbers thus obtained are given in Table III, the chlorine water here used not being saturated, but containing 0·002192 gram Cl per c.c. All the experiments, except the last one, were performed in weak diffused daylight; the amount of hydrochloric acid formed, however, does not appear to be increased to any great extent by the action of light.

TABLE III.—*Showing the Loss of Chlorine produced by Heating Chlorine Water.*

Chlorine water taken.	Temperature.	Time.	Thiosulphate required.	Loss of free chlorine experienced.
50 c.c. . .	Before heating	—	25·98	—
" "	"	—	26·01	
" "	"	—	26·03	
" "	"	—	26·02	
" "	Heated to 100° C. and cooled slowly	about $\frac{1}{4}$ hr.	24·94	24·99 c.c.
" "	"	"	25·04	
" "	At 100° C.	for $\frac{1}{4}$ hr.	24·48	24·435 c.c.
" "	"	for 1 hr.	24·39	
" "	"	"	23·61	23·635 c.c.
" "	"	"	23·58	
" "	"	"	23·67	
" "	"	"	23·68	
" "	"	for 2 hrs.	22·37 c.c.	14·00 "
" "	At 62° C.	for 1 hr.	24·81 c.c.	4·63 "
" "	" 41 "	"	25·28 "	2·80 "
" "	" 20 "	for 2½ hrs.	24·62 "	0·22 " per hr.
" "	"	"	24·89 "	0·18 " "
	in the dark			

These experiments show that a very considerable loss of free chlorine takes place at 100°, and also at lower temperatures,* being quite sufficient to account for the loss experienced in Bunsen's method, especially as the chlorine is then in a nascent condition; and, that

* Some chlorine water was heated over mercury that the oxygen liberated might be collected; in place, however, of this gas being evolved, the mercury was oxidised, an oxychloride being probably formed. When some mercury was shaken with strong chlorine water it was converted at once into a fine grey powder, which, on subsiding, left the liquid quite colourless. Lead immersed in chlorine water became oxidised immediately, the metal, and especially the parts of the glass vessel near it, becoming coated with a film of what appeared to be lead dioxide.

this is the true explanation of this loss is supported by the fact that the results obtained are lower in proportion as more prolonged boiling is necessary to liberate the chlorine, *i.e.*, the results are lower as the acid used is more dilute, and also lower in the case of potassium bichromate than with manganese oxide. Nor can any of this loss be considered as mechanical, for, if it were so, it would be extremely improbable that an entire change in the apparatus used should not alter its amount, and impossible that no loss should take place when undiluted acid is employed for the solution of the oxide.

§ IV. *Conclusion.*—It hence appears that Bunsen's method is capable of yielding accurate results only in the case of manganese oxides, using the strongest acid. The modification of it here investigated has the advantage of being, not only accurate, but far more expeditious and less troublesome than the original method; a smaller quantity of acid being required (2 to 5 c.c. for a determination), and the correction due to the iodine liberated by this acid being determinable with greater ease and certainty than in Bunsen's process. Unfortunately, however, it has the disadvantage of not being applicable to manganese ores, since the ferric oxide present in them would also liberate iodine from the potassium iodide, and therefore in these cases Bunsen's method must be employed, using all the precautions here indicated.

XIV.—*A New and Simple Apparatus for the Treatment of Substances in Open Dishes by Volatile Solvents.*

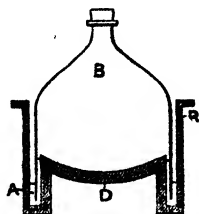
By A. WYNTER BLYTH.

It is often a matter of great convenience to treat a substance in an open dish with ether, benzene, or other volatile solvent, but hitherto no more effective appliance for the prevention of waste and inconvenience has been used than covering the dish with a funnel or watch-glass.

The little apparatus which I have now used for more than a year effectually converts the dish into a closed vessel, so that ether and volatile liquids can now be boiled in an open dish for an hour without loss, or, on the other hand, a volatile liquid can be distilled off and recovered with as much ease as in operating with a retort.

The essential part of the apparatus consists of a cast iron body, R, externally drum-shaped, and having a deep groove, A, in which a little mercury, M, or other "sealing liquid" is placed. Into this groove fits a bell-jar, B, and the part marked D is hollowed out for

the reception of a dish. The size of the dish is quite indifferent; any dish will do so long as it is not too large for the bell-jar to cover. The neck of the bell-jar is attached to a Liebig's condenser.



Should a substance require exhaustion with the solvent, the Liebig is placed in an upright position; should an evaporation or distillation be required, the condenser is placed in the usual slanting position, and in this way all the liquid evaporated is saved. As a matter of convenience it is well to have a pair of these apparatuses in a laboratory, one with an upright, the other with a slant condenser.*

XV.—*On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State.*

By T. E. THORPE, Ph.D., F.R.S.

ON attempting to trace the development of our knowledge concerning the connection which exists between the weights of unit volumes of liquid substances and their relative molecular weights, it will be found that practically nothing had been gained prior to the publication of Hermann Kopp's well known memoirs. Indeed but little was practicable until the necessity of comparing the liquids when under strictly analogous conditions had been recognised as a fundamental condition of the comparison. By dividing the specific gravities of liquids taken at the temperatures at which their vapour-tensions are equal to the standard atmospheric pressure—that is, at their ordinary boiling points—into their molecular weights, certain comparable values are obtained which are known as specific volumes. If the specific gravities are referred to water at 4° C., these values represent the number of cubic centimetres occupied by the relative molecular weights of the liquids, expressed in grams, at their respective boiling points under the standard pressure. Thus the specific volume of water is 18·8, which may be taken to

* The apparatus can be obtained from Messrs. Cetti, Brook Street, Holborn.

mean that 18 grams of water at 100° occupy 18.8 c.c. The numbers so obtained were first shown by Kopp to exhibit certain definite relations, which may be briefly indicated as follows:—

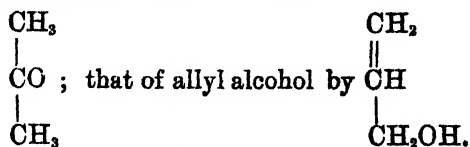
1. *In many instances differences in specific volume are proportional to differences in corresponding chemical formulæ.* Thus a difference of CH_2 in a homologous series corresponds to a difference of about 22 in the specific volume, or $(\text{CH}_2)x = 22x$. On comparing the specific volumes of similarly constituted haloïd compounds, it is seen that the substitution of n atoms of bromine for an equal number of chlorine atoms increases the specific volume by $5n$.

2. *Isomeric and metameric liquids have, as a rule, the same specific volume.* Exceptions, to be referred to hereafter, are exhibited by certain oxygen and sulphur compounds.

3. *The substitution of an atom of carbon for two of hydrogen makes no alteration in the specific volume of members of certain groups of organic liquids.*

It would seem to follow from Kopp's observations that the specific volume of a liquid formed by the union of two other liquids is equal to the sum of the specific volumes of its components. It may also be inferred that the members of the same family of elements possess identical specific volumes: thus the common value of phosphorus, arsenic, and antimony would appear to be about 27; that of silicon, titanium, and tin would seem to be about 35.

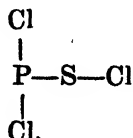
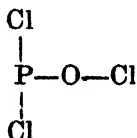
On the basis of these conclusions Kopp was able to calculate certain fundamental values for the specific volumes of the elements in combination. These values are as a rule constant for the particular element: thus carbon has invariably the value 11, hydrogen that of 5.5. Exceptions are observed in the case of the chemical analogues oxygen and sulphur. Each of these bodies has two values depending, it would seem, on its mode of combination, or on its relation to the remaining atoms in the molecule. For example, acetone and allyl alcohol have each the empirical formula $\text{C}_3\text{H}_6\text{O}$, but the specific volume of acetone is 78.2, whilst that of allyl alcohol is 73.8. The constitution of acetone may be expressed by the formula—



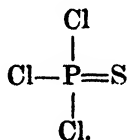
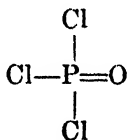
In the case of acetone the affinities of the oxygen are wholly satisfied by the carbon, that is, we have reason to think that the oxygen atom is more intimately associated with one of the carbon atoms than it is with any one of those of the other element, whereas in allyl alcohol a moiety of the combining value would seem to be satisfied by carbon and

the remainder by hydrogen. It appears then, that when oxygen is united to an element by both its affinities its specific volume is 12.2; when it is attached by only one combining unit its specific volume is 7.8. The corresponding values for sulphur are 28.6 and 22.6.

I have already pointed out (*Proc. Roy. Soc.*, 160, 1875) how these differences in the values for the specific volumes of oxygen and sulphur may be employed to throw light upon the constitution of such bodies as phosphoryl trichloride and thiophosphoryl trichloride. If the phosphorus in these substances be regarded as trivalent, they must possess the constitution—



If, on the other hand, the phosphorus is pentavalent, they must be written—



It is obvious that the knowledge of the specific volumes of PCl_3 , POCl_3 , and PSCl_3 will serve to indicate the mode of combination of the oxygen and sulphur, and hence to determine the atomic value of the phosphorus in these compounds, provided that the specific volume of the phosphorus is invariable, or is independent of its atomic value. This is merely one of the many instances that might be adduced to show that a knowledge of the specific volume of a body is often calculated to furnish valuable information concerning its constitution.

The specific volume of nitrogen also appears to be variable. According to Kopp, in the amines it is 2.3; in cyanogen and certain nitro-compounds it is about 17. No rational explanation of this difference has yet been given. In fact some observations recently published by Dr. Ramsay (*Chem. Soc. J.*, No. cci, 473) seem to give widely different values for the specific volume of nitrogen in different amines, and appear also to show that this element has a distinct value in the pyridine series of bases. On the supposition that the atomic value of an element is variable, Buff has suggested (*Ann. Chem. Pharm.*, Suppl., 4, 129) that its specific volume is a function of that value, but the experimental evidence which he has adduced in support of this proposition is not very definite. So far as we know, however, there is no *a priori* reason why oxygen, sulphur, and nitrogen should alone possess variable specific volumes.

Of late years a fresh interest has accrued to the whole question, on account of the intradependence which has been shown to exist between the atomic weight of an element and its chemical and physical characteristics, specific volume included. Our information on this latter point is at present extremely imperfect, but so far as it goes it would seem to indicate that the specific volumes, like the other physical and chemical properties of the elementary bodies, are periodic functions of their atomic weights.

Among the many problems suggested by a review of our present knowledge of the subject, the following seem to me to be specially worthy of solution:—

- I. Is it definitely established that an element in combination has as a rule an invariable specific volume? May not the volume be modified by the number of the atoms of that particular element in the molecule? Is it altogether independent of the general complexity of the molecule, or may not the specific volume of the molecule be a function of its weight?
- II. Do the various members of a given family of elements possess identical specific volumes, or may not the volume be a function of the atomic weight?
- III. Would a re-examination of the cases of so-called variable atomic value serve to show that the specific volume of an element is a function of that value, as Buff supposes?
- IV. The hypotheses of Mendelejeff and Meyer indicate the need for additional and more exact determinations of the values for the specific volumes of the elementary bodies.
- V. Lastly it is desirable to multiply examples of the aid afforded by a knowledge of the specific volume of a compound in elucidating its constitution.

With a view of solving these and certain other points of inquiry which will be referred to hereafter, I drew up a scheme of work which involved the determination of the specific volume of the following 52 liquids:—

Bromine	Br_2 .
Iodine monochloride	ICl .
Ethylene bromide	$\text{C}_2\text{H}_4\text{Br}_2$.
Ethylene chloriodide	$\text{C}_2\text{H}_4\text{ICl}$.
Ethylene chloride	$\text{C}_2\text{H}_4\text{Cl}_2$.
Ethidene chloride	$\text{C}_2\text{H}_4\text{Cl}_2$.
Acetyl chloride	$\text{C}_2\text{H}_3\text{OCl}$.
Trichloroacetyl chloride	C_2OCl_4 .

Chloral	$C_2Cl_3OH.$
Pentachlorethane	$C_2HCl_5.$
Methene chloride	$CH_2Cl_2.$
Chloroform	$CHCl_3.$
Chloropicrin	$C(NO)_2Cl_3.$
Carbon tetrachloride	$CCl_4.$
Chloracetoneitrile.....	$CCl_3CN.$
Bromoform	$CHBr_3.$
Trichlorobromomethane.....	$CBrCl_3.$
Ethyl cyanide	$C_2H_5.CN.$
Propionitrile	$C_2H_5.CN.$
Epichlorhydrin	$C_3H_5OCl.$
Allyl alcohol.....	$C_3H_5O.$
Acetone.....	$C_3H_6O.$
Heptane	$C_7H_{16}.$
Ethylamyl	$C_7H_{16}.$
Octane	$C_8H_{18}.$
Di-isobutyl	$C_8H_{18}.$
Aniline	$C_6H_7N.$
Picoline.....	$C_6H_7N.$
Mono- or triethylamine ..	$NH_2C_2H_5,$ or $N(C_2H_5)_3.$
Nitrogen tetroxide	$N_2O_4.$
Silicon tetrachloride	$SiCl_4.$
Titanium tetrachloride	$TiCl_4.$
Tin tetrachloride	$SnCl_4.$
Phosphorus trichloride	$PCl_3.$
Phosphorus tribromide	$PBr_3.$
Phosphoryl chloride	$POCl_3.$
Thiophosphoryl chloride.....	$PSCl_3.$
Phosphoryl bromochloride.....	$POBrCl_3.$
Vanadyl trichloride.....	$VOCl_3.$
Ethoxyphosphorus chloride	$PCl_2.C_2H_5O.$
Triethylphosphine	$P(C_2H_5)_3.$
Phosphenyl chloride	$PClC_6H_5.$
Arsenic trifluoride	$AsF_3.$
Arsenic trichloride	$AsCl_3.$

Antimony trichloride	SbCl ₃ .
Thionyl dichloride	SOCl ₂ .
Sulphothionyl chloride	SSCl ₂ .
Sulphurylhydroxyl chloride	SO ₂ OHCl.
Sulphuryl dichloride	SO ₂ Cl ₂ .
Disulphuryl chloride	S ₂ O ₂ Cl ₂ .
Chromyl dichloride.....	CrO ₂ Cl ₂ .
Carbon disulphide	CS ₂ .

This list might without doubt have been greatly extended, and in several important directions. One essential consideration in the choice of particular liquids for investigation was the possibility of obtaining them in a state of purity. I was anxious too to exclude as far as possible all liquids boiling above 200°, on account of the difficulty of accurately determining their rates of expansion at high temperatures.

The results of the observations made with these substances will afford material for the determination of the specific volumes of the following 17 elementary bodies.

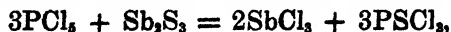
	Atomic weight.		Atomic weight.
Hydrogen.....	1·0	Nitrogen	14·01
		Phosphorus.....	30·96
Fluorine	19·0	Vanadium	51·2
Chlorine	35·37	Arsenic.....	74·9
Bromine	79·75	Antimony	120·0
Iodine	126·53		
		Carbon.....	11·97
Oxygen.....	15·96	Silicon.....	28·0
Sulphur.....	31·98	Titanium.....	48·0
Chromium.....	52·4	Tin	117·8

1. METHODS OF OBSERVATION.

Preparation of the Liquids. Modes of ascertaining their Purity.—In the preparation of the liquids employed in this research, I have whenever possible preferred to make use of methods which would directly yield the wished-for substance unmixed with any other product, or if that were not practicable I have sought to arrange that the bye-products should be such as could be removed with certainty. All processes of fractional distillation are comparatively valueless for the preparation of liquids of a high degree of purity. Hence in the preparation of such a liquid as thiophosphoryl chloride I have chosen to make use of the reaction—



rather than employ Baudrimont's method, based on the action of phosphorus pentachloride upon antimony tersulphide—

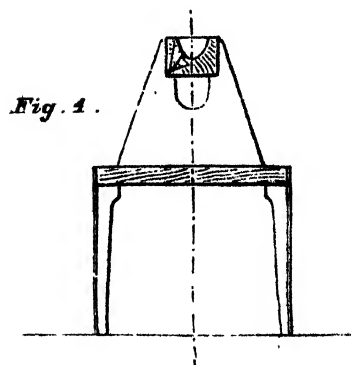
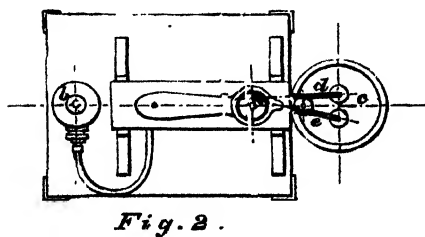
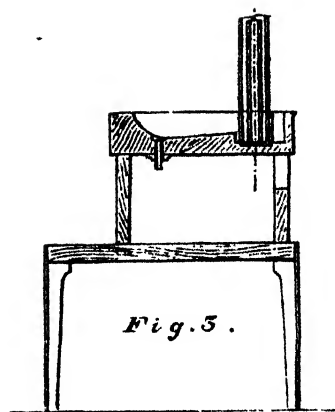
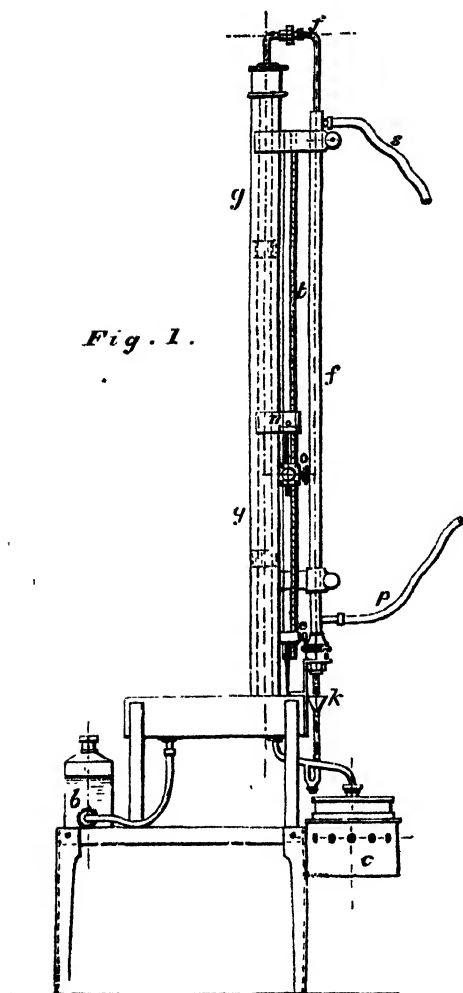


which would involve a separation by distillation.

Whenever the mode of preparation was not a sufficient guarantee of the purity of the liquid, as of course happened not unfrequently, I have sought to establish this either by analysis or by the determination of its vapour-density. In the case of the inorganic liquids, which were mainly chlorides or bromides readily decomposed by water, this was usually effected by estimations of the amount of the halogen. For the greater number of the organic compounds the method of vapour-density was employed. Indeed in a number of instances the ordinary methods of organic analysis would be of very little avail in determining the purity of the compounds. Thus an organic combustion as ordinarily made gives practically no clue to the purity of such a substance as heptane. This body may be mixed with 20 per cent. of its next higher or lower homologue without affecting the analytical results beyond the errors incidental to the method. In cases of this character the determination of the molecular weight from the vapour-density affords not only the most accurate but also the readiest mode of ascertaining the degree of purity.

As the greater number of the organic compounds given in the foregoing list were of comparatively low boiling point, the Gay-Lussac-Hofmann method was generally applicable. The form of the apparatus employed by me differs slightly from that in general use: as it admits of all the precision which the process is capable of yielding, it may be desirable to describe it in full. It is represented in Figs. 1—4, about $\frac{1}{10}$ th the actual size.

The trough, seen in plan in Fig. 2, and in section at Figs. 3 and 4, is made of bay-wood. It is 200 mm. long and 70 mm. broad, and holds about 200 c.c. of mercury. The cavity or well is 50 mm. in diameter, and about 12 mm. deep, measured from the ledge. This trough can be completely filled with mercury or emptied by raising or lowering the bottle, *b*, Fig. 1, which is connected with the trough by a stout caoutchouc tube. By "kinking" the tube as the mercury flows out, the metal may be kept at any desired level in the trough. The trough is rounded at the bottom in order to economise the mercury, and from its shape allows all the metal to flow out into the bottle when this is lowered, with the exception of that contained in the well below the ledge. Through the bottom of the well pass two nickel-plated brass tubes 8 mm. in diameter, which are connected with the boiler, *c*, by means of screws: one of them, *d* (Fig. 2), stands 11 mm., and the other, *e*, 8 mm. above the mercury in the well: *e* passes down nearly to



the bottom of the boiler; *d* (Fig. 2), ends immediately below the upper surface of the boiler. The boiler itself holds about 1,000 c.c., and is less than quarter filled with the liquid (water, aniline, &c.) employed to vaporise the substance under investigation. The vapour-density tube is 950 mm. long, and 16 mm. in internal diameter: it is not graduated, but has a thin mark etched round it at about 35 mm. from the upper end. It is surrounded by the wider tube, *gg*, 36 mm. in diameter and 960 mm. long: this is surmounted by a brass cap, and is connected with the condenser, *ff*, by a flanged screw. The steam or aniline-vapour passes from the wide tube into the condenser, the lower end of which terminates above the funnel *k*, so that the condensed liquid flows back into the boiler. The water required for the condenser flows in at *p* and passes out through *s*. Attached to the condenser, which is made sufficiently rigid to serve as a support for the tubes, is a brass bar, *t*, in a slot in which works a brass scale divided into millimetres, and at the lower end of which is a steel pointer. This scale with the attached pointer can be moved up and down by means of the rack and pinion seen at *e*, so as to make the pointer just touch the level of the mercury in the well. At *n* is an arrangement to assist in determining accurately the level of the mercury in the vapour-density tube. It consists of a semicircular strip of brass working vertically along the outer tube. By tightening a screw behind *o*, and working the rack and pinion at *o*, the lower edge of the strip can be brought into exact coincidence with the level of the mercury in the inner tube, and its height from the level of that in the trough, that is, from the end of the steel pointer, read off on the graduated brass scale.

The capacity of the vapour-density tube above the etched mark is determined once and for all by weighing with mercury in the ordinary way: in the tube actually used it was 64.155 c.c. at 0°. The lower part of the tube is then calibrated by pouring in successive equal volumes of mercury as in Bunsen's method of calibrating an eudiometer, and the position of the mercury after each addition is read off on the graduated scale. Knowing the capacity of the little measuring tube employed to fill in the mercury, we obtain the value in cubic centimetres corresponding to each millimetre of the vapour-density tube below the etched mark, exactly as in an eudiometer. The results are incorporated in a table which gives directly the volume in the tube at every millimetre below the fixed mark.

To make a vapour-density determination by means of this apparatus, the brass tubes *d* and *e* (Fig. 2) are connected together at the ends in the trough, by a piece of caoutchouc tube, and the trough is nearly filled with mercury by raising the bottle *b*, and "kinking" the tube. The vapour-density tube is next carefully filled with mercury, and the weighed quantity of the liquid experimented upon is introduced in the

ordinary way in a small stoppered tube or bottle. The vapour-density tube is then brought into the well, the bottle *b* lowered so as to empty the trough to the level of the ledge, the caoutchouc tube connecting *d* and *e* (Fig. 2) removed, a wedge of cork slipped over the vapour-density tube, and the outer glass tube placed in position and put into connection with the condenser. It will be seen from Fig. 2 that the two brass tubes *d* and *e* are now between the glass tubes. The lamp is then placed beneath the boiler, when the vapour of the liquid passes up by *d*; that which condenses between the glass tubes flows back by *e*, whilst the excess passes out at the top, and condensing in the tube surrounded by cold water flows back through the funnel *k* connected with *e* into the boiler. When the height of the flame beneath the boiler is properly arranged, the apparatus will work for hours, if necessary, with perfect regularity and without requiring any attention. As the mercury flows out from the vapour-density tube, it falls over the ledge of the well and runs into the bottle. As soon as the volume of the vapour is constant, the pointer is brought into coincidence with the level of the mercury in the well, and the position of the fixed mark and then the level of the mercury in the tube are determined on the brass millimetre scale.

The latter reading gives at once the height of the mercury column in the vapour-density tube, and the difference between the two readings gives the number of millimetres below the fixed mark, and hence the volume of the vapour as shown in the calibration table. The height of the barometer is then determined, or it may be obtained with sufficient accuracy by a preliminary reading of the height of the mercurial column in the vapour-density tube before the introduction of the weighed quantity of liquid: from this we can calculate the temperature of the steam, if water be employed in the boiler, with approximate accuracy, by the simple expression—

$$t = 100^{\circ} + 0.0375 (h - 760),$$

in which *h* is the barometric height at the time of observation; or obtain it at once from the accompanying Table:—

T°.	Barom. mm.	Diff.	T°.	Barom. mm.	Diff.	T°.	Barom. mm.	Diff.
98.5	720.2	2.6	99.2	738.5	2.7	99.9	757.3	2.7
98.6	722.8	"	99.3	741.2	"	100.0	760.0	"
98.7	725.4	"	99.4	743.8	"	100.1	762.7	"
98.8	728.0	"	99.5	746.5	"	100.2	765.5	2.8
98.9	730.6	"	99.6	749.2	"	100.3	768.2	"
99.0	733.2	"	99.7	751.9	"	100.4	771.0	"
99.1	735.9	2.7	99.8	754.6	"	100.5	773.7	"

If any other liquid be used, it is best to tie a thermometer to the

vapour-density tube before the larger tube is placed over it, and to read off the temperature at the moment that the volume of the enclosed vapour is determined.

The method of calculation calls for very little explanation. The volume of the vapour is corrected for the error of the meniscus; this in a tube of the dimensions given was found to be 0.41 c.c.; and for the expansion of the glass, taken as .000025 for 1° C., and the height of the mercurial column is reduced to the standard temperature by Mendelejeff's extremely convenient formula—

$$V_t = 1 + .00018t + .00000002t^2.$$

The height of the barometer is at the same time reduced to 0° by the ordinary tables.

It is unnecessary to make any correction for the tension of the mercury-vapour at about 100°: at temperatures much above this, it must, of course, be taken into account. At 132° (boiling point of amyl alcohol) it is 2.1 mm.; at 160° (boiling point of oil of turpentine) it is 5.9 mm.; at 183° (boiling point of aniline) it is 11.8 mm.; at 200° it is 19.9 mm.

It will be seen that the vapour required to heat the liquid is introduced from below, and that the vapour-density tube has no etched scale upon it; these two circumstances greatly diminish the risk of cracking the tube. Moreover, the whole mass of the mercury within the tube is uniformly heated to a known temperature, and therefore its reduction to 0° can be made with accuracy. The quantity of the metal which is needed is comparatively small, not exceeding 300 c.c.: and the amount of the liquid in the boiler should not be more than 150 c.c. Numerous examples are given in this communication showing the degree of accuracy which the method is capable of affording, and I may refer to my paper entitled "A Contribution to the Theory of Fractional Distillation" (*Chem. Soc. J.*, August, 1879), for an illustration of its value in determining the proportion of the constituents of a mixed liquid which can be volatilised without action on mercury.

In order to ascertain the specific volumes of liquids we require to know their specific gravities under comparable conditions of temperature, and, in accordance with Kopp's suggestion, the temperature of the boiling point of the particular liquid under standard pressure is usually adopted. How far liquids are strictly comparable under these conditions will be discussed hereafter. The direct determination of the specific gravity of the liquid at its boiling point cannot be readily made with the highest degree of accuracy. Dr. Ramsay has recently described a very simple method which admits of a fair approximation to exactitude, and by means of this apparatus he has determined the specific volumes of a considerable number of substances (*Chem. Soc.*

J., loc. cit.). I have preferred to adopt the principle of the method already employed by Kopp: that is (1) to determine the specific gravity of the liquid at some convenient temperature; (2) to ascertain its boiling point with the utmost exactitude; and (3) to determine with great care its rate of expansion, say between 0° and the boiling point.

By operating in this manner and by making use of methods of well established value, my work would serve to put on record a number of accurately determined physical data of great importance, and I should be adding to the material required for a discussion of the laws regulating the thermal expansion of liquids, even if the main object of my investigation were not attained.

I proceed, therefore, to describe the apparatus and methods of observation necessitated by the three distinct series of operations.

The Thermometers.—Two sets of thermometers were employed: the first set made by Casella consisted of three instruments varying from -9° to 160° ; each instrument was graduated into tenths of a degree, and each scale division of 0.1° had a length of about 1 mm.: the second set was made by Geissler of Bonn; it also comprised three thermometers graduated like the others, and extending from -14° to 170° , 1° on these instruments was about 6 mm. in length. Both sets were compared previous to use, with Kew standards, made by the late Mr. Welsh, and the divergences were tabulated and applied as corrections in the subsequent observations. I am indebted to Sir William Thomson, in whose possession the standards are, for the opportunity of making the comparison. At a later period of the research the Casella thermometers were carefully calibrated by Bessel's method as modified by von Cettingen, and were employed in the comparison of the air and mercurial thermometers undertaken by me in conjunction with my colleague Professor Rücker.

In the course of the investigation, a large number of determinations of the fixed points of all the instruments have been made, and, as usually happens, these were found to rise gradually in each case, although not to the same extent in all. The position of the lower fixed point was determined, after heating, whenever practicable, in snow; at other times in finely powdered well-washed ice.

The upper point was determined by the aid of the apparatus devised by Regnault for this purpose, the temperature of the steam being calculated from his tables from the atmospheric pressure at the time of observation. The readings in all cases were made by means of a telescope provided with cross-hairs and micrometer screw. The degree of permanent displacement may be seen from the following examples of observations made on the Casella instruments: the results are in all cases means of a large number of readings.

Therm. A.		Therm. B.	
Dec., 1873	— 0·07	Nov., 1873	— 0·04
Jan., 1874	— 0·00	Dec. 3, „	+ 0·03
April, „	+ 0·02	„ 4, „	+ 0·06
June, „	+ 0·03	„ 6, „	+ 0·09
Nov., „	+ 0·04	Jan., 1874	+ 0·12
June, 1875	+ 0·04	April, „	+ 0·15
June, 1876	+ 0·05	Feb., 1875	+ 0·20
Nov., „	+ 0·07	June, „	+ 0·23
Jan., 1877	+ 0·09	Jan., 1876	+ 0·25
May, „	+ 0·10	April, 1877	+ 0·26
Nov., 1878	+ 0·09	Nov., 1878	+ 0·21
Jan., 1879	+ 0·09	Dec., 1879	+ 0·23
March, „	+ 0·08	Jan., 1880	+ 0·21
Oct., „	+ 0·07		
Jan., 1880	+ 0·07		

Therm. C.	
Nov., 1873	+ 0·10
April, 1874	+ 0·13
Feb., 1875	+ 0·20
May, „	+ 0·28
April, 1877	+ 0·40
June, „	+ 0·47
Nov., 1878	+ 0·43
Dec., 1879	+ 0·43

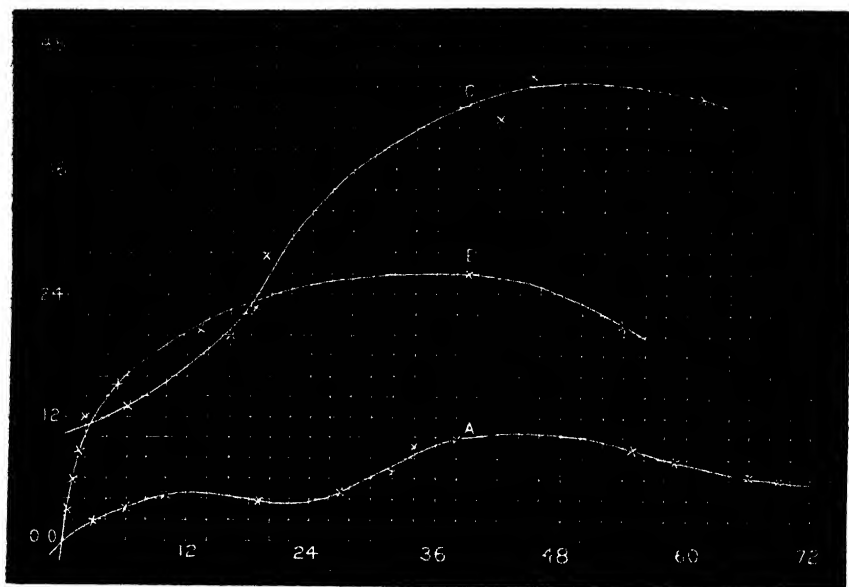
The extent of the displacement is evidently dependent on, or at any rate is greatly influenced by, the degree of heating, or in other words by the amount of molecular disturbance to which the glass envelope is subjected; this seems to confirm the opinion of Legrand and W. H. Miller, that it is not solely due, as generally supposed, to the influence of atmospheric pressure on the glass.

The rise in the fixed points is graphically represented in Fig. 5, the abscissæ represent the times, in months, at which the several observations were taken, and the ordinates the extent of displacement in hundredths of a degree.

The curve of B strikingly resembles one deduced from Despretz's observations of the change in zero-point of a particular instrument in his possession: the comparatively unsymmetrical character of the others is probably owing in great part to the irregular expansion and contraction which, as Matthiessen has shown, is frequently exhibited by glass exposed to alterations of temperature.*

* The bulbs of these thermometers were sealed to the stems. Verdet says, "Dans les thermomètres dont le réservoir a été soudé à la tige, on observe un déplacement plus considérable que dans les thermomètres dont les réservoir a été soufflé."

Fig. 5.—CURVES SHOWING RISE OF FIXED POINTS IN THERMOMETERS.



Unless otherwise stated, all temperatures are expressed in air-thermometer degrees, which are distinguished, in order to prevent confusion, by the symbol Δ .*

The conversion from the ordinary scale was made by the aid of a table compiled from the observations of Recknagel (*Pogg. Ann.*, 123) for temperatures below 100° , and from those of Regnault made with a thermometer of ordinary glass for temperatures above that point. The following abstract of the table is given in order to allow of the reconversion to the ordinary scale if desired :—

Table for Conversion of Mercurial Thermometer Degrees into those of the Air Thermometer.

Mercurial thermometer.	Air thermometer. Δ .	Mercurial thermometer.	Air thermometer. Δ .
0°	0.00	80°	79.90
10	9.92	90	89.95
20	19.86	100	100.00
30	29.82	110	110.03
40	39.80	120	120.06
50	49.81	130	130.08
60	59.82	140	140.12
70	69.86	150	150.20

* Δ = Bergman's symbol for fire or heat.

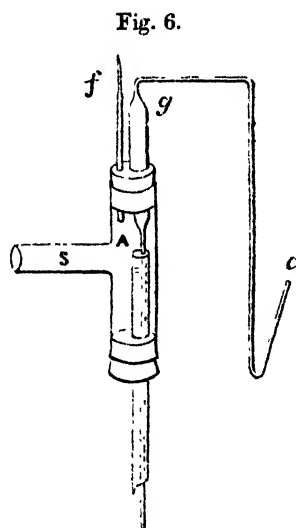
The Dilatometers.—The dilatometers were purposely constructed of flint glass for the reason that the expansion of this variety of glass is considerably less than that of soda or of hard glass, and as Pierre and Matthiessen have shown, its rate is much more uniform.*

The stem of each instrument was about 50 centimetres long, and it was graduated in millimetres: the bulbs had a capacity of from 2 to 4 c.c. We have, of course, no reason to suppose that these bulbs are not liable to changes in capacity similar to those noticed in the case of the thermometers, but as the following determinations, made at various times during the space of a couple of years, on a somewhat larger bulb in constant use, show, such changes are too small to exercise any sensible influence on the results:—

	Weight of water at 4° contained in bulb.
April, 1875.....	4.61195 grams
May, „	4.61185 „
Nov., 1876	4.61176 „
April, 1877.....	4.61176 „

In the case of the dilatometers, the risk of any considerable amount of change was still further reduced by repeatedly heating and cooling the bulbs before determining their capacities. The number of times was not actually counted, but it exceeded several hundreds in every case. It is known that the effect of these alterations of temperature is to bring the glass into a condition of molecular equilibrium analogous to that which it is supposed to take up in a thermometer after prolonged use.

In order to determine their capacity, and to calibrate their stems, the dilatometers were first carefully cleaned, dried, and weighed, and then completely filled with pure mercury by the aid of the apparatus represented in Fig. 6.



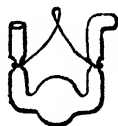
* The glass had a specific gravity of 2.832, and an analysis made for me by one of my former students, Mr. G. Johnstone, showed that it had the following composition:—

Silica.....	55.88
Lead oxide	33.63
Iron and alumina.....	1.09
Potash	9.67

100.27

The glass tube A was fitted with caoutchouc corks previously well soaked in melted paraffin: through the lower one was passed the dilatometer, through the upper one were inserted two tubes, *f* and *g*, the former of which was sealed at the upper point; *g* was drawn out at each end into long capillary tubes, the upper length being bent twice at right angles, as shown in the figure, and sealed at the point *e*; the other end was made sufficiently long and fine to pass down the stem of the dilatometer into the bulb. The tubes being in place, and the outer surfaces of the corks again covered with melted paraffin, the side-tube was connected in the ordinary manner with the Sprengel pump, and the whole arrangement exhausted as completely as possible, the flow of the mercury being continued for a couple of hours after the height of that in the fall-tube was practically identical with that of the barometer. A small beaker containing the pure and warm mercury was then brought under *g*, and raised until the greater portion of the tube was submerged, the point *e* was then broken off, when the mercury immediately rushed over into the bulb of the dilatometer, and gradually filled the whole instrument, the pump being meanwhile continuously worked. As soon as the mercury flowed from the end of the dilatometer, the point of *f* was broken in order to admit the air and the action of the pump was stopped. The apparatus was then disconnected, and the capillary tube of *g* carefully withdrawn from the dilatometer. This mode of filling such instruments with mercury is readily executed, and is far preferable to the ordinary method of expelling the air by boiling the metal. The dilatometer filled with mercury was again weighed and then placed in a bath of water of known temperature, and the height of the mercurial column determined in the ordinary way by the telescope. In order to calibrate the stem, successive lengths of the mercurial column were removed by suction through a fine capillary tube inserted into the stem and ending in the small bulb apparatus (Fig. 7) previously weighed.

Fig. 7.



The increase in the weight of the apparatus gave the amount of mercury so withdrawn; its length in the stem was read off on the graduated scale, the fractions of the millimetre being determined by the aid of the micrometer screw of the telescope. Experience showed that it was better to empty the bulb after each weighing than to retain the mercury in the apparatus, since the volatilisation of the metal caused an

appreciable loss of weight in the course of a few hours. During the entire process, the dilatometer was surrounded by water of nearly constant temperature flowing directly from the main. The following readings made in the course of the calibration of dilatometer N may serve as an example of the character of the variations observed:—

Scale reading.	Mean point.	Temp. C. Degrees.	Length abstracted in mm.	Weight of mercury. Grams.	Mean value of 1 div. in grams of mercury.
262.39	242.34	5.46	40.11	0.5569	.01389
222.28	206.89	5.45	30.79	0.4201	.01364
191.49	166.10	5.44	50.78	0.6864	.01352
140.71	126.93	5.45	27.56	0.3709	.01346
113.15	95.93	5.45	34.44	0.4656	.01352
78.71	63.63	5.46	30.17	0.4113	.01363
48.54	29.06	5.48	38.96	0.5400	.01387
9.58	—3.34	5.49	25.83	0.3588	.01390
—16.25					

It will be noticed that the diameter of the tube becomes gradually less from division 242 to 127, after which it slowly increases. This is a fair sample of what was usually observed: although the tubes were carefully selected in the first instance, a number of them being tested preliminarily by the ordinary method of propulsion of a short column of mercury, I was unable to obtain them, in the lengths required, of uniformly increasing or diminishing bore; and a subsequent examination, made with the greatest care by the method of propulsion of a number of tubes of still finer bore, has convinced me that it is but very rarely that the variation in the diameter of the capillary tubes of greater length than 20 centimetres can be properly expressed by formulæ of the kind employed by Kopp.

After the greater portion of the mercury in the stem had been withdrawn, the dilatometer was again weighed; the average of the mean values of the mercury contained in a division was then taken, and that number representing the weight of the unit-volume was divided into the weight of the mercury contained in the bulb together with that in the stem up to the zero-point. The ratios of the mean weights of the mercury contained in one division in various portions of the stem to the weight of the unit-volume were then determined, the intermediate values being obtained by interpolation, and from these a calibration table showing the number of unit-volumes corresponding to each division on the scale was constructed.

In the course of the investigation I have in this way made and calibrated nine dilatometers of varying capacities, respectively designated as A, B, C, D, E, M, N, O, and P. The bulbs of A, B, and C were blown directly from the tube; those of D and E were sealed on to the stem; M and N were fitted with glass stopcocks; O and P were of

considerable capacity, and their bulbs were cylindrical and comparatively narrow. The weight of the unit-volumes in mercury varied from 0·01054 in the case of O to 0·01556 in that of E. Their several capacities in unit-volumes were:—

A.....	1600·19	M.....	3383·03
B.....	2851·60	N.....	3383·84
C.....	2964·70		
D.....	3283·42	O.....	6182·72
E.....	2868·25	P.....	6174·41

In order to determine the expansion of the glass the dilatometers partially filled with mercury, after the final weighings in the calibration, were placed in melting ice or in water of known temperature, and the position of the mercury in the stem accurately determined; the instruments were then heated by steam from boiling water in the apparatus employed to determine the upper fixed point of the thermometers, the temperature of the steam being calculated from the barometric pressure, and the position of the mercury column again read. The mean results for 1° between 0° and 100° were:—

A.....	·0000251	M.....	·0000244
B.....	·0000254	N.....	·0000254
C.....	·0000247		
D.....	·0000213	O.....	·0000252
E.....	·0000230	P.....	·0000248

The comparatively small expansions of D and E are possibly connected with the fact that the bulbs of these instruments were sealed on to the stems, and not blown directly out of the tube: indeed in the case of D two such sealings were made near the bulb, as the stem was accidentally broken in the course of the calibrations. The separate results in the case of D were:—(1), ·0000214; (2), ·0000212; (3), ·0000213.

Determination of the Boiling Points of the Liquids.—The liquids were invariably redistilled immediately preceding the determination of their specific gravities and rates of expansion, and the boiling points were ascertained in the final distillation. Special care was taken to avoid superheating; and whenever the nature of the liquid permitted, a spiral of platinum wire was placed in the flask to prevent succussive boiling. As the thermometers employed were of unusual length, it was not always practicable to immerse the mercurial column entirely in the vapour; hence the correction for the cooled portion of the thread became at times of considerable importance.

As Holtzmann has already pointed out, the well-known expression—

$$\delta (t-t')n,$$

in which t = the observed temperature on the thermometer; t' the mean temperature of the cooled column as determined by an attached thermometer; n the length of the cooled column expressed in degrees; and δ = the apparent expansion of mercury in glass for 1° , viz., $\cdot000154$; over corrects the results especially at high temperatures: at 200° the error amounts to $0\cdot5^\circ$. For temperatures at about the boiling point of water the error is not very considerable, although it can be perceived by careful reading. The following observations were made in the apparatus employed to determine the upper fixed points of the thermometers.

n .	t' .	t .	Actual temperature.	Calculated temperature.		
				δ $\cdot000154$	δ $\cdot000135$	δ $\cdot000143$
20	$27\cdot5$	$99\cdot92$	$100\cdot09$	$100\cdot14$	$100\cdot11$	$100\cdot12$
40	$24\cdot5$	$99\cdot70$	„	$100\cdot16$	$100\cdot11$	$100\cdot13$
60	$21\cdot9$	$99\cdot42$	„	$100\cdot14$	$100\cdot05$	$100\cdot09$
80	$21\cdot3$	$99\cdot20$	„	$100\cdot16$	$100\cdot04$	$100\cdot09$
20	$25\cdot5$	$99\cdot86$	$100\cdot09$	$100\cdot09$	$100\cdot06$	$100\cdot07$
40	$25\cdot6$	$99\cdot68$	„	$100\cdot14$	$100\cdot08$	$100\cdot10$
134	$38\cdot0$	$133\cdot5$	$135\cdot4$	$135\cdot5$	$135\cdot2$	$135\cdot3$
161	$35\cdot0$	$161\cdot0$	$163\cdot9$	$164\cdot12$	$163\cdot7$	$163\cdot9$
196	$42\cdot0$	$196\cdot2$	$200\cdot4$	$200\cdot9$	$200\cdot3$	$200\cdot5$
218	$51\cdot0$	$218\cdot0$	$223\cdot1$	$223\cdot6$	$222\cdot9$	$223\cdot2$
166	$53\cdot0$	$246\cdot0$	$250\cdot4$	$250\cdot9$	$250\cdot3$	$250\cdot6$

It will be seen that in all cases where the value of δ is taken as $\cdot000154$, the results are over corrected.

Landolt and Wüllner (*Ann. Chem. Pharm.*, Suppl., **8**, 1867), and more recently Mills (*Chem. News*, **31**, 234), have discussed the various modes of correcting for the cooled column, and the former observers have proposed to substitute for Kopp's simple expression a far more complicated formula, based on observations made with thermometers of Geissler's pattern, to which it is more directly applicable than to those which were most frequently employed by me. Perhaps the simplest mode of approximating to the actual temperature is to follow Holtzmann's example, and to modify the value of δ in the formula. The number adopted by Holtzmann is $\cdot000135$, but, as Landolt and Wüllner have shown, this number gives uniformly low results when n is greater than 60, and $t - t'$ exceeds 75 . Mills found that δ was about $\cdot00013$, and increased $\cdot00001$ for every additional 25° . In fact $\delta = \alpha + \beta n$. Although it would doubtless have been more rigorously accurate to have determined the values of α and β for the several instruments, I find from a large number of observations that

the mean value $\cdot 000143$ gives sufficiently accurate results for all temperatures up to 200° , and for all values of n which are likely to occur in practice. The numbers in the final column of the preceding table have been calculated by the use of this constant: it will be seen that they agree very satisfactorily with the actual numbers contained in the fourth column. As the table of corrections calculated by this constant differs slightly from that generally used, it may be desirable to reproduce it here:—

Table for the Correction of Thermometer Readings.

T - t.	n.									
	10	20	30	40	50	60	70	80	90	100
10	0·01	0·03	0·04	0·06	0·07	0·09	0·10	0·11	0·13	0·14
20	0·02	0·06	0·09	0·11	0·14	0·17	0·20	0·22	0·26	0·29
30	0·04	0·09	0·13	0·17	0·21	0·26	0·30	0·34	0·39	0·43
40	0·05	0·11	0·17	0·23	0·28	0·34	0·40	0·47	0·52	0·57
50	0·07	0·14	0·21	0·29	0·36	0·43	0·50	0·60	0·64	0·71
60	0·08	0·17	0·25	0·35	0·43	0·51	0·60	0·70	0·77	0·86
70	0·10	0·20	0·30	0·40	0·50	0·60	0·70	0·80	0·90	1·00
80	0·11	0·23	0·34	0·45	0·57	0·68	0·80	0·91	1·03	1·14
90	0·13	0·26	0·39	0·51	0·64	0·77	0·90	1·03	1·16	1·30
100	0·14	0·28	0·43	0·57	0·71	0·85	1·00	1·14	1·29	1·43
110	0·16	0·31	0·47	0·63	0·79	0·94	1·10	1·26	1·42	1·58
120	0·17	0·34	0·51	0·69	0·86	1·03	1·20	1·37	1·54	1·71

T - t.	n.									
	110	120	130	140	150	160	170	180	190	200
10	0·16	0·17	0·19	0·20	0·21	0·22	0·24	0·26	0·27	0·29
20	0·31	0·34	0·37	0·40	0·43	0·46	0·49	0·51	0·54	0·57
30	0·47	0·51	0·56	0·60	0·64	0·68	0·73	0·77	0·82	0·86
40	0·63	0·69	0·74	0·80	0·86	0·91	0·97	1·03	1·09	1·14
50	0·79	0·86	0·93	1·00	1·07	1·14	1·22	1·29	1·36	1·43
60	0·94	1·03	1·12	1·20	1·29	1·37	1·46	1·54	1·63	1·72
70	1·10	1·20	1·30	1·40	1·50	1·60	1·70	1·80	1·90	2·00
80	1·26	1·37	1·49	1·60	1·72	1·83	1·94	2·05	2·17	2·29
90	1·42	1·54	1·66	1·80	1·93	2·05	2·17	2·31	2·45	2·54
100	1·58	1·71	1·84	2·00	2·15	2·29	2·43	2·57	2·72	2·86
110	1·73	1·89	2·04	2·20	2·36	2·51	2·67	2·83	2·99	3·15
120	1·89	2·06	2·23	2·40	2·57	2·74	2·92	3·09	3·26	3·43

The barometer employed was a standard instrument on Fortin's pattern, and had been verified at Kew. All barometric readings are corrected and reduced to 0° . In order to make them as nearly comparable as possible, the boiling points corrected for the error of the cooled column are reduced to the standard pressure of 760 mm. by means of the expression $\cdot 0375 (h - 760)$, in which h is the height of the barometer at the time of observation.* This expression, of course, assumes the validity of Dalton's law, but the error introduced is negligible. In two or three cases I have calculated the corrected boiling points from vapour-tension observations when these have been at hand, but the difference between the results thus obtained and those given by the above formula has never exceeded $0\cdot 05^{\circ}$; hence we may assume that for the ordinary barometric variations the formula is generally applicable.

Determination of Specific Gravity.—The bottles employed had a capacity of from 4 to 20 c.c., and were fitted with ground glass stoppers. As already pointed out by Kopp, other things being equal, there is a probable gain in accuracy in the use of bottles of comparatively small capacity; the disadvantage that smaller differences in the relative weights are obtained as compared with the larger flasks being more than counterbalanced by the rapidity and certainty with which the liquid acquires a constant temperature. I have preferred to use stoppered bottles to the Sprengel apparatus on account of the special character of many of the liquids.

All the weighings were made by the method of vibrations and are reduced to a vacuum. The weights employed were an excellent set made by Staudinger, of Giessen, and had been verified with great care. The specific gravities were usually taken at the temperature of melting ice, and are compared with water at 4° . In cases where reductions were necessary they were made by the formula—

$$S_0 = S_t \frac{V'}{V},$$

in which S_0 = the specific gravity at 0° .

S_t = " " the higher temperature t .

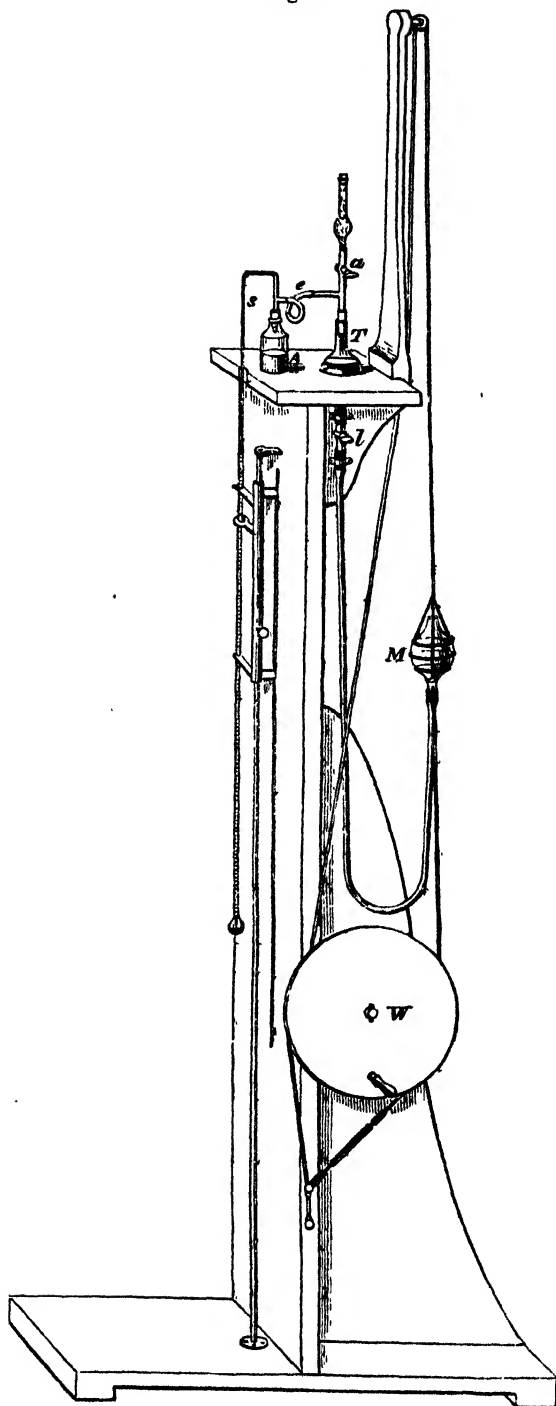
V' = the volume of the liquid at t , obtained by the interpolation formulæ.

V = the volume of the water at t (vol. at $4^{\circ} = 1$), from Rossetti's tables.

Determination of the Thermal Expansion of the Liquids.—As many of

* The Yorkshire College is in lat. $53^{\circ} 48'$ and 186 feet above the sea-level. No attempt has been made to reduce the observations to a standard atmosphere. The height of the barometer corresponding to the standard atmosphere in Leeds is 759·427 mm. at 0° .

Fig. 8.



the liquids experimented upon were strongly fuming corrosive substances, readily decomposed by atmospheric moisture, it was scarcely possible to introduce them into the dilatometers in the ordinary way without the risk of slight alteration. The arrangement adopted in the case of these bodies is seen in Fig. 8; it was found so convenient in practice that it was employed generally even when working with liquids for which it was not originally designed. The liquid was distilled, with the proper precautions to exclude moisture, directly from the flask in which its boiling point had been determined into the bottle A, which was fitted with a caoutchouc cork containing a short length of glass tube, through which was inserted the fine capillary tube *s*, passing down the stem and into the bulb of the dilatometer. Before connecting the caoutchouc tube *e*, the vessel T was filled with mercury, and the glass stopcock *l* being closed, M was lowered as indicated in the figure, and the cocks *a* and *l* slowly opened; the mercury in the upper vessel ran down into M and air dried by passing over pumice moistened with oil of vitriol contained in the drying tube, flowed into T. As soon as the mercury ceased to run the cocks *a* and *l* were turned, and M was raised by a couple of turns of the wheel W up to the pulley. The cock *l* was opened when the pressure exerted by the mercury drove the liquid from A over into the dilatometer. The flow was so slow that it was easy to regulate the height in the stem to any wished-for position, by gradually lowering the brass frame carrying the dilatometer as the liquid passed over. Just before the required quantity had been admitted *l* was closed and *a* opened; the flow of the liquid still continued but with great slowness, the long leg of the capillary tube acting as a syphon. M was then brought back to its original position, and *a* was closed and the dilatometer lowered until the end of the capillary tube was at the point in the stem at which it was desired that the liquid should stand; the cock *l* was again opened, and the liquid in the capillary tube quickly drawn back into A, when *a* was opened to prevent the passage of the air through the tube into the liquid. It was found to be quite unnecessary to close the ends of the dilatometers during the process of filling, as the extent of surface exposed by the liquid to the air was too small to cause any sensible decomposition. By a simple and obvious modification, by which the entire apparatus could be filled with dry carbon dioxide or hydrogen, it would be possible to make use of this arrangement in the case of liquids like zinc- and cadmium-ethyl, which ignite in contact with oxygen.

The same apparatus was used to transfer the liquid to the specific gravity bottles; these were usually filled immediately after the dilato-

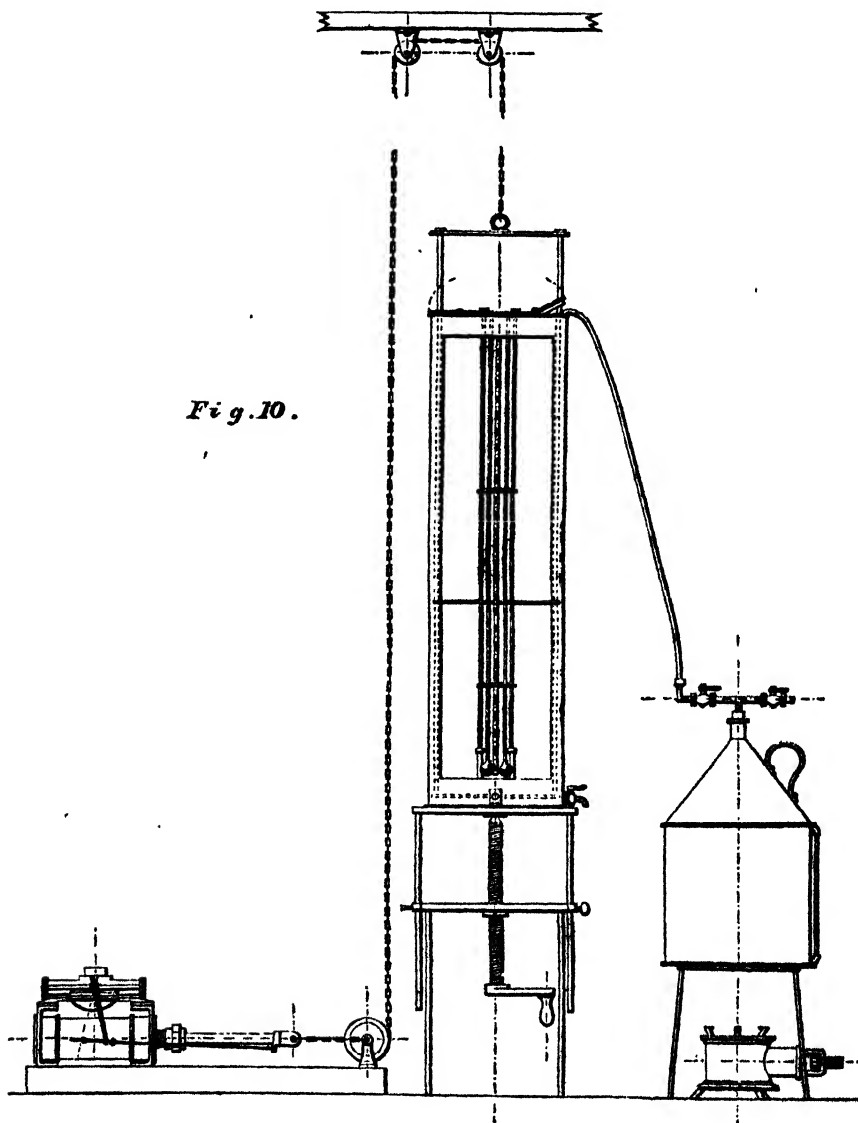
Fig. 9.



meters. Fig. 9 shows the mode in which the bottles were supported on the sliding frame.

The dilatometers thus charged were closed with glass rods with ground ends and plunged into oil, heated to within a few degrees of the boiling point of the liquid. Occasionally and more particularly in the case of the readily decomposable inorganic chlorides, a few minute bubbles of gas formed in the liquid during the preliminary heating: these were easily driven up the stem by gently tapping the instrument. The dilatometers were then momentarily unclosed, to liberate the air

Fig. 10.



compressed in the stem above the liquid, and the glass rods again put into position and firmly fastened down on the ground end of the dilatometer by strong caoutchouc tubing and copper wire. Of course in the case of the dilatometers provided with stopcocks, the manipulation was even simpler. After standing from 16 to 20 hours at the ordinary temperature the dilatometers were placed in melting ice, and in about an hour the position of the liquid at 0° was determined by the aid of the telescope. At the same time the zero point of the thermometer was ascertained.

The dilatometers and thermometer were then placed in a brass frame, and immersed in water contained in a large copper bath (Fig. 10), fitted with plate glass sides and standing on an iron table, the height of which could be adjusted by a screw.

The bath held about 22 litres of water, which could be kept in constant motion by stirrers, worked by a small hydraulic engine. Direct experiments proved that the temperature of the various portions of the water never differed more than by $.05^{\circ}$. The little engine (for which I am indebted to my friend, Mr. Henry Davey, C.E.), was under perfect control and did its work admirably: it entirely dispensed with the necessity for an assistant. The water of the bath was gradually heated by steam blown in from a boiler, and the current could, if necessary, be so regulated that the temperature of the bath could be maintained at any desired point between 30° and 60° to within 0.05° for practically any length of time.

In order to facilitate the subsequent calculation of the empirical formula expressing the rate of expansion, the readings were taken at twelve approximately equidistant temperatures between 0° and the boiling point of the liquid. Up to about 25° the temperature of the water could be maintained absolutely constant, but at points higher than this it was found better to take a series of readings with a slowly ascending and descending temperature than to spend time in attempting to obtain it perfectly uniform. As soon as the temperature of the water of the bath approached the desired point the current of steam was regulated so as to cause a very slow and gradual increase in temperature, and a series of readings was taken on the two instruments. The current of steam was still further reduced or altogether stopped as the case required, and as the temperature slowly fell a second series of readings was taken, equal in number to the first, and the mean of the double series was considered to represent the uncorrected temperature and volume of the liquid. The readings were made by the telescope, furnished with cross hairs and a micrometer screw, placed at a distance of about four feet from the bath: 44 divisions on the screw corresponded to one division on the dilatometer, and the readings could be made with certainty to the $\frac{1}{44}$ th of a unit-volume. The

following readings taken indiscriminately from the note book serve to show the general character of the observations:—

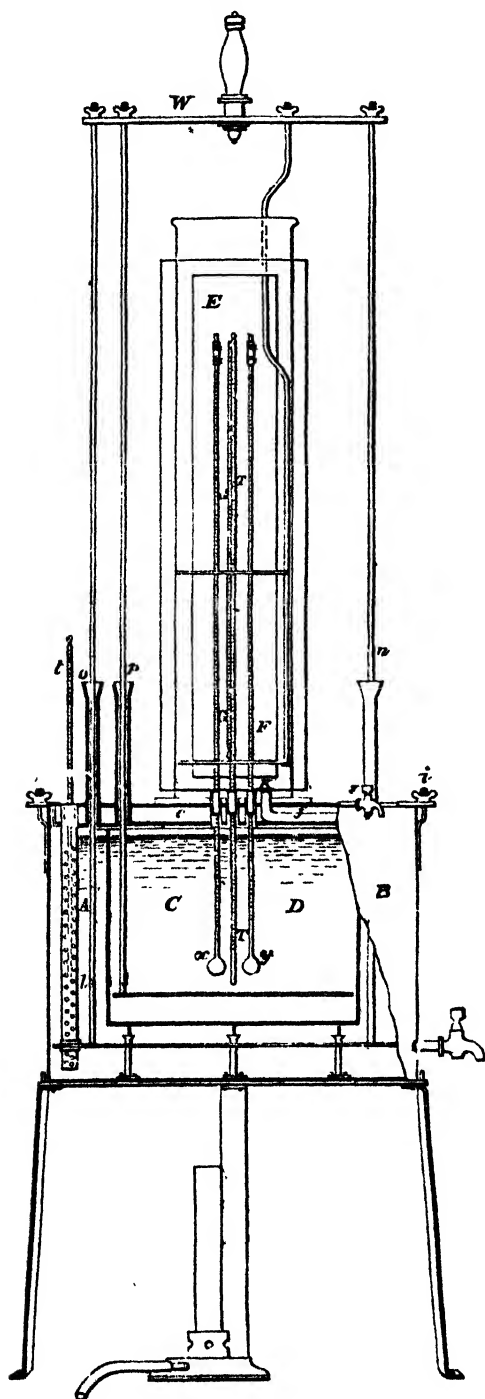
Temperature.	Scale reading on dilatometer.
47·32°	125·39
47·37	125·43
47·38	125·47
47·40	125·57
47·38	125·57
47·35	125·48
47·31	125·41
Mean 47·36°	125·47

As a rule the liquids were not heated beyond 65° in the water-bath, partly on account of the difficulty of maintaining the large bulk of water of an approximately constant temperature, but more especially from the length of time and large quantity of steam needed to heat the water above this point. The succeeding observations were therefore made in the apparatus represented in Fig. 11.

AB is a cylindrical bath, made of sheet iron and holding about 25 litres; in it is placed a second bath, CD, of 10 litres capacity, resting on three short stout rods fitting into tubes fastened to the bottom of the outer-bath: both baths were filled with cotton-seed oil. The lid, *ef*, when in position, is fixed to the bath by screws, *iii*; it carries a wide brass tube, *l*, open at the bottom and pierced with holes; this serves to protect the thermometer, *t*, which indicates the temperature in the outer bath; the three brass tubes, *o*, *p*, *n*, act as guides to the rods of the stirrers. In order to keep the oil in the upper bath, EF, as cool as possible, and more especially to avoid any rapid changes in its temperature, the lid, *ef*, is made double; as the various tubes passing through it are soldered to both sides, the intermediate space is practically an air chamber. EF is a rectangular frame fitted with plate-glass sides; it is fitted to a flange which can be screwed down on to the top of the lid. It was filled with almost colourless rape oil, which could be withdrawn when necessary by the tap, *s*, communicating with the tube *k*. The dilatometers, *x* and *y*, carrying tightly-fitting brass tubes stuffed with small leather discs and tapped with screws, were screwed on to the bottom plates of the lid, the thermometer, T, being passed through the lid from above and held in position by a precisely similar arrangement; the thermometer, G, fastened to T, served to indicate the temperature of the bath, EF, and hence that of the cooled columns in the thermometer and dilatometers. The oil in all the baths was kept in constant motion by stirrers connected with the cross bar, W, and worked by the small engine.

In order to make an observation, the oil in the outer-bath was heated

Fig. 11.



a few degrees higher than the desired point, the exact number of degrees depending upon the temperature needed in the internal bath. The flame of the lamp below the bath was then either removed or lowered as the case demanded, and as the thermometer, T, became nearly stationary from the extreme slowness with which the heat was communicated from the outer to the inner bath, a series of readings was taken in the following order:—(1) of the thermometer, T; (2) of the dilatometer; (3) of the thermometer, G; (4) of the dilatometer; (5) of the thermometer, T; (6) of the thermometer, G; the readings being continued in this order with a gradually ascending and descending temperature, as in the water-bath observations.

The following example of a set of readings will more clearly illustrate their character:—

T.	G.	Dilatometer scale reading.
89.50	28.6	328.10
.51	.6	.34
.52	.7	.59
.55	.7	.63
.53	.7	.70
.51	.7	.66
.48	.8	.63
.42	.8	.52
Mean.. 89.50	28.7	328.52

As was anticipated, and as is evident both from this and from the former example, the thermometer is far more sensitive to changes of temperature than the dilatometer; but by the method of reading with a slowly ascending and descending thermometer, any error which might have been due to this cause is practically eliminated. It is unnecessary to read G to nearer than 0.2° , but as the thermometer actually used was graduated to tenths, the temperature was always observed to the nearest scale division.

Reduction of the Observations.—In his observations Kopp also employed a double oil-bath, but the capacity of the baths (glass beakers) was very much smaller than in the apparatus above described. Moreover, the stems of the dilatometers and thermometers were for the greater part of their length simply surrounded by air, of which the temperature at about the middle part of the exposed stems, as determined by an attached thermometer, was assumed to be that of the mean temperature of the columns. The true volume was calculated by successive approximations by means of the expression—

$$V_T + E \frac{V_T - V_t}{V_t},$$

in which V_T is the observed volume in the dilatometer at T , E the length of the exposed and cooled column measured in scale divisions, from the surface of the oil in the inner bath to the level of the liquid in the stem, t the mean temperature of this column, and V_t the volume of the liquid in the dilatometer at t . The correction thus obtained was added to V_T and the result V_T inserted in the above expression, and the calculation repeated until no sensible alteration was obtained.

Direct experiments have shown that this method of correcting the observed volumes tends to give too high results, from the circumstance that the liquid in the exposed portions of the stem has a uniformly higher temperature than the mean temperature of the air. A dilatometer was filled with water and the level of the liquid carefully determined at various temperatures between 18° and 25° in the water-bath, and it was then heated by steam in the apparatus employed to determine the upper fixed points of the thermometers. The dilatometer was placed so as to expose varying lengths of the stem containing water to the air, and the temperature of the middle point of the cooled column was determined by an attached thermometer exactly in the manner described by Kopp, and with all the precautions adopted by him to prevent overheating and to avoid sudden changes in the temperature t .

The results were as follows:—

V_T .	t .	E .	V_t .	Calculated vol.
3301.2	0.0	0.0	0.0	—
3298.3	23.2	83.3	3177.8	3301.5
3296.1	22.7	144.9	3177.5	3301.6
3293.0	22.6	220.8	3177.4	3301.7
3290.6	22.3	286.4	3177.2	3301.8
3288.5	21.2	338.2	3176.6	3301.8

It will be noticed that the calculated volumes are in all cases in excess of that directly observed, viz., 3301.2.

By reducing the value of E by $10 + .015 E$ in each case, results may be obtained which agree almost exactly with the true volume. The calculated values are respectively—

3301.2
3301.3
3301.1
3301.2
3301.2

The mean of these values is identical with the true value.

From a large number of experiments made with several liquids at various temperatures, and with different lengths of cooled columns, I find that in my apparatus, E may be taken as the whole length of the column in the upper bath, expressed in scale divisions.

The corrected volumes have been calculated by the formula—

$$\frac{V_T - E}{V_t - E} V_t,$$

in which V_T , V_t , and E have the same significance as in Kopp's formula.

The rate of expansion, from 0° to the boiling point, of all the liquids experimented upon by me may be represented with sufficient accuracy by a single expression of the form—

$$V = A + Bt + Ct^2 + Dt^3,$$

the values of the constants being found by substituting successively for V and t the twelve corresponding values observed at equidistant points between 0° and the boiling point of the liquid, and adding together the resulting expressions in consecutive groups of three, so as to form four equations of condition, by solving which the four unknown quantities were determined. Each coefficient was then divided by A , giving an expression of the form—

$$V = 1 + B't + C't^2 + D't^3.$$

Correcting for the expansion of the glass, δ , of the particular dilatometer employed, this becomes—

$$V = 1 + (B' + \delta)t + (C' + B'\delta)t^2 + (D' + C'\delta)t^3,$$

which will be hereafter referred to under the form—

$$V = 1 + at + bt^2 + ct^3.$$

The labour of reducing the observations, and more especially of calculating the empirical formulæ for so large a number of substances, has been very considerable, and it is but just that I should acknowledge my indebtedness to my wife for her assistance in this matter: aided by the arithmometer of Thomas (de Colmar)—an instrument of the greatest service in calculations of this kind—she undertook the greater portion of the very tedious work of computation. I would also here express my obligations to my colleague, Professor Rücker, for his aid in the mathematical portion of the research.

Before beginning the proper work of the investigation I made a series of observations on water, mainly with the view of obtaining information concerning the degree of accuracy of my method of experiment. The very careful discussions which have been made from time to time, particularly by Miller, Matthiessen, and Rossetti, of the numerous observations already published, made by methods widely divergent in principle, go to prove that the rate of expansion of this liquid is known with almost absolute certainty. Moreover, I imagined that these preliminary observations would incidentally serve to show how

far the objection which has been urged against the dilatometrical method by Matthiessen that it tends to give uniformly low rates of expansion is well founded. Two dilatometers, B and C, were charged with recently boiled distilled water in the manner already described. When cold they were put into melting ice for an hour, and the levels read with the following results:—

B 3051·05
C 3172·06

The bulbs were then placed in hot water; the liquid in B expanded through about 100 divisions, that in C through about 107 divisions; when nearly cold the instruments were again placed in melting ice and the levels again read—

B 3051·08
C 3172·10

After standing for 70 hours the levels were—

B 3051·08
C 3172·13

These observations show that no error due to the liquid adhering to the walls of the tube is to be feared, and that the method of closing the dilatometers effectually prevents all evaporation of the liquid.

The results of the observations of the expansion are shown in the following table, and are compared with the mean results of the observations of Kopp, Pierre, Despretz, Hagen, Matthiessen, Kremers,

Temp.° C.	Dilatometer.		Relative volumes corrected for expansion of glass.		Mean.	X.	Y.
	B.	C.	B.	C.			
0·00	3051·08	3172·13	1·00000	1·00000	1·00000	1·00000	1·00000
9·70	3050·67	3171·78	1·00011	1·00013	1·00012	1·00010	1·00012
11·99	3051·17	3172·27	1·00034	1·00034	1·00034	1·00032	1·00036
15·00	3052·21	3173·29	1·00075	1·00073	1·00074	1·00071	1·00074
18·52	3053·82	3174·85	1·00136	1·00132	1·00134	1·00132	1·00139
21·50	3055·41	3176·77	1·00197	1·00199	1·00198	1·00194	1·00200
24·96	3057·63	3178·95	1·00279	1·00277	1·00278	1·00275	1·00283
28·20	3059·98	3181·63	1·00364	1·00370	1·00367	1·00361	1·00370
31·83	3063·22	3184·67	1·00479	1·00475	1·00477	1·00468	1·00479
36·10	3067·35	3189·11	1·00626	1·00625	1·00625	1·00612	1·00627
45·21	3077·54	3199·55	1·00983	1·00978	1·00980	1·00967	1·00980
54·45	3089·58	3212·21	1·01403	1·01400	1·01401	1·01398	1·01397
63·69	3103·55	3226·81	1·01885	1·01883	1·01884	1·01878	1·01890
72·67	3118·57	3242·60	1·02401	1·02405	1·02404	1·02406	1·02412
81·71	3135·48	3260·37	1·02980	1·02989	1·02986	1·02986	1·02993
90·80	3154·04	3279·80	1·03614	1·03626	1·03620	1·03610	1·03618

Weidner, and Rossetti in column X, and in column Y with the means of the fairly-accordant results of Matthiessen and Hagen made by the method of displacement.

My own results agree rather better with those of Hagen than with those of Matthiessen, which are generally higher than those of previous investigators. The differences, however, are far too inconsiderable to throw any doubt on the validity of the dilatometrical method of determining the thermal expansions of liquids.

I proceed now to give the details of the mode of preparation and purification of the several liquids, and the results of the observations made to determine their boiling points, specific gravities, and rates of expansion by heat. I have at the same time collected together, so far as I could, all previously existing information on these points, and I have in many cases reduced the observations in order to make them more strictly comparable with my own.*

II.—SPECIFIC GRAVITIES, BOILING POINTS, AND RATES OF THERMAL EXPANSION OF THE VARIOUS LIQUIDS.

Bromine, Br₂.

About a kilogram of commercial bromine was carefully dehydrated by agitation with pure concentrated sulphuric acid, and distilled, the fraction boiling at about 60°, which amounted to nearly two-thirds of the whole, being collected separately. A portion of the distillate was treated with milk of lime and ammonia, and the resulting calcium bromide was tested for iodine, according to the method employed by Stas, but not a trace was found. The remainder of the bromine was placed over powdered potassium bromide, and after several months' digestion, it was again distilled, and the distillate agitated with phosphorus pentoxide to remove the last traces of water.

The purified bromine boiled constantly at 59·47° under a pressure of 765·2 mm. ($n = 0$, $t = 0$). Reduced and corrected boiling point, 59·27°.

The specific gravity was found to be 3·15787 at 9·10°, compared with water at the same temperature; at 0°, compared with water at 4°, it is 3·18828. According to Pierre, bromine boils at 63° under a pressure of 760·32 mm., and has a specific gravity of 3·18718 at 0°.

* Some of the observations here given have been published in preliminary form in a couple of papers contributed to the *Proceedings of the Royal Society*, No. 167, 1876. The details of final results are now however given for the first time.

compared with water at 4°* (*Ann. de Chim. et de Phys.* [3], 20). Bolas and Groves found 59·6° under a barometric pressure of 751 mm.

The following observations of the expansion were made with Dilatometer C:—

In the water-bath:—

T ^Δ .	Observed.	Calculated.	T ^Δ .	Observed.	Calculated.
0·00	3006·7	3006·8	21·70	3076·9	3077·0
5·53	3024·2	3024·2	27·00	3094·8	3094·9
10·68	3040·8	3040·7	32·29	3112·9	3113·2
16·29	3059·2	3059·0			

In the oil-bath:—

T°.	t°.	T ^Δ .	V.	E.	Observed.	Calculated.
32·50	17·9	32·37	3111·6	115·0	3113·5	3113·3
38·36	20·4	38·24	3131·1	134·4	3133·7	3133·7
43·66	21·8	43·59	3148·6	151·9	3152·3	3152·5
48·87	23·0	48·84	3166·2	169·5	3171·1	3171·3
54·64	23·2	54·58	3185·2	188·5	3191·9	3192·1
59·38	24·5	59·36	3201·7	205·1	3210·0	3209·6

These observations may be represented with sufficient accuracy by the formula—

$$3006·767 + 3·119\ 46t + 0·005\ 567t^2 - 0·000\ 094\ 14t^3,$$

by means of which the volumes in the last columns of each of the foregoing tables have been calculated.

On dividing through by the first term and correcting for the expansion of the glass (0·0000247), we obtain the following formula as expressing the expansion of bromine between 0^Δ and its boiling point:—

$$V = 1 + 0·001\ 062\ 18t + 0·000\ 001\ 877\ 14t^2 - 0·000\ 000\ 003\ 085t^3.$$

The following table shows the true volume of bromine at every 5^Δ between 0^Δ and 60^Δ, the volume at 0^Δ being taken as 100000:—

* Pierre's determinations of boiling points are generally higher than those given by subsequent observers: this fact is in all probability due to the circumstance that they were made with the thermometer bulb in the liquid.

$\Delta C.$	Volume.	Diff.	$\Delta C.$	Volume.	Diff.
0	100000	—	40	104529	595
5	100536	536	45	105132	603
10	101081	545	50	105742	610
15	101635	554	55	106359	617
20	102197	562	60	106983	624
25	102768	571			
30	103347	579	53.27	1.06911	—
35	103934	587			

The rate of expansion of bromine has already been determined by Pierre, who has given the following expression to represent the results of his observations:—

$$V = 1 + 0.001\,038\,186\,255t + 0.000\,001\,711\,380\,853t^2 + 0.000\,000\,005\,447\,118t^3.$$

This formula gives numbers agreeing fairly well with those afforded by the expression deduced from my observations, as the following comparison shows:—

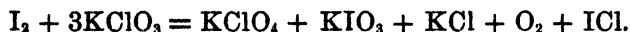
	15°.	30°.	45°.	60°.
Pierre	1.01608	1.03273	1.05068	1.06963
Thorpe.	1.01624	1.03326	1.05108	1.06960

Pierre has undoubtedly the credit of having first determined the specific gravity and thermal expansion of approximately pure bromine; but it seems probable, in spite of the care which was evidently taken in its preparation, that the sample employed by him in his observations was not perfectly free from water. This, indeed, is indicated by the order of the divergence between the results of our observations; and the supposition would seem to be confirmed by the high solidifying point, viz., -7.5 to -8° , which he noticed. Baumhauer finds the true freezing point of bromine to be -24.5° (*Ber.*, 1871, 927). Pierre attempted to dehydrate the bromine by digestion with calcium chloride. According to Stas (*Nouvelle's Recherches sur les lois, &c.*, Aronstein's Transl., 179), calcium bromide (which as a desiccating agent is not inferior to the chloride) is incapable of removing the last trace of water from bromine.

Iodine Monochloride, ICl.

This remarkable substance has nearly the same molecular weight as bromine, and, when liquid, bears considerable resemblance to that element. It may be prepared by the direct union of iodine and chlorine, but is more conveniently obtained by heating an intimate

mixture of iodine and potassium chlorate, and distilling the product from powdered potassium chlorate.



A large quantity of the compound prepared in this way boiled constantly, after repeated distillation, between 99.7 and 100.7° , $n = 40$, $t = 25^\circ$. Bar., 744.3 mm. Corrected and reduced boiling point, 101.3° .

Iodine monochloride has been variously described as a reddish-brown oily liquid (Gay-Lussac), and a hyacinth-red crystalline solid (Schützenberger). Both statements are correct. After distillation, especially if kept in sealed tubes, the monochloride will remain liquid for many weeks, even in a freezing mixture. On the addition of a minute trace of the terchloride, solidification at once ensues. A quantity of the liquid monochloride, placed in an open tube, solidifies after a few days, owing to the conversion of a portion of the monochloride into the terchloride and free iodine: $3\text{ICl} = \text{ICl}_3 + \text{I}_2$. Hannay (*Chem. Soc. J.*, 1873, 815), and more recently Bornemann (*Annalen*, 1877, 183), have already made a number of interesting observations on the causes which induce the solidification of this substance. I find the monochloride melts at 24.2° ; Hannay found 24.7° , Trapp and also Bornemann, 25° .

Analysis showed that the substance obtained by the above reaction was pure iodine monochloride. Bulbs containing weighed portions of the liquid were broken under dilute sulphurous acid solution, and the hydrochloric and hydriodic acids were precipitated by silver nitrate, and the mixed silver salts digested with nitric acid. The results were as follows:—

I. Amount of ICl taken	1.2482 grams
II. " " 	0.5668 "
I. Silver salts obtained	2.9095 grams
II. " " 	1.3223 "

From the formula

$$W = \frac{\text{I} + \text{Ag}}{\text{I}} x + \frac{\text{Cl} + \text{Ag}}{\text{Cl}} y,$$

in which W is the weight of mixed silver salts, and x and y the amount of iodine and chlorine respectively contained in them, we find the percentage composition of the monochloride to be:—

	I.	II.	Calculated.
Chlorine	21.86	21.98	21.85
Iodine	78.14	78.02	78.15
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00
			n 2

A determination of the specific gravity of this compound gave 3.12988 at 17.95°, compared with water at 4°; at 0° its specific gravity is 3.18223, also compared with water at 4°.

The following observations on the rate of expansion were made with Dilatometer C in the water-bath:—

ΔC.	Observed.	Calculated.	ΔC.	Observed.	Calculated.
0.00	2997.6	2997.6	53.70	3149.1	3149.3
9.24	3022.5	3022.5	62.73	3176.8	3176.8
17.69	3045.8	3045.7	71.73	3204.9	3204.8
26.73	3070.9	3070.9	80.70	3233.1	3233.3
35.91	3097.1	3097.1	89.82	3263.2	3263.1
44.65	3122.5	3122.5			

The observations may be accurately represented by the formula

$$2997.609 + 2.67146t + 0.0024309t^2 + 0.000008183t^3,$$

by means of which the numbers in the third column are calculated.

Dividing through by the first term and correcting for the expansion of the glass (.0000247); we obtain the following formula, as expressing the true expansion of iodine monochloride between 0° and its boiling point:—

$$V = 1 + 0.000915896t + .00000083296t^2 + .00000002750t^3.$$

By means of this formula, the following table has been calculated:—

ΔC.	Volume.	Diff.	ΔC.	Volume.	Diff.
0	100000	—	55	105335	513
5	100460	460	60	105855	520
10	100925	465	65	106381	526
15	101394	469	70	106914	533
20	101867	473	75	107454	540
25	102346	479	80	108001	547
30	102830	484	85	108556	555
35	103320	490	90	109118	562
40	103815	495	95	109689	571
45	104315	500	100	110267	578
50	104822	507	101.3	1.104187	—

Ethene Dibromide, C₂H₄Br₂.

This compound was prepared by passing a stream of well-washed ethene through pure bromine under water, treating the resulting oil with dilute soda solution, and distilling, after dehydration, with phos-

phorus pentoxide. The entire amount of liquid boiled between 130.1 and 130.8° ; on redistillation, the greater portion came over between 130.6 and 130.7° , $n = 55$, $t = 11.3^{\circ}$. Bar., 766.6 mm. Corrected and reduced boiling point, 131.45^{Δ} .

The recorded observations on the freezing point of ethene dibromide are very discordant; they vary from as low as -12 or -15° to as high as $+13.1^{\circ}$. I found that my preparation solidified at $+9.2^{\circ}$, which is almost identical with Regnault's number, 9.53° .

Its specific gravity was found to be 2.19011 at 10.89° , compared with water at 4° . On the assumption that the liquid contracts regularly below its ordinary solidifying point, its specific gravity at 0° is 2.21324 , compared with water at 4° .

Other observers have found for the boiling and freezing points and specific gravity of this compound:—

	Boiling point.	Melting point.	Specific gravity.
Regnault	131.6 at 760 mm.	9.53°	—
Pierre	132.6 „ 756.9 „	13.1	2.16292 at 20.79°
Haagen	131.6 „ ?	—	2.1827 „ 20°
Cahours	130 ?	0	—
Reboul	— —	—	2.198 „ 10°

Observations on the rate of expansion made with Dilatometer C gave the following results:—

In the water-bath:—

T^{Δ} .	Observed.	Calculated.	T^{Δ} .	Observed.	Calculated.
9.82	2973.7	2973.8	53.92	3101.6	3101.7
20.85	3004.6	3004.7	65.11	3136.4	3136.3
31.98	3036.8	3036.6	76.33	3171.8	3172.0
43.00	3068.9	3068.9			

In the oil-bath:—

T° .	t° .	T^{Δ} .	V.	E.	Observed.	Calculated.
65.32	20.5	65.22	3130.4	147.7	3137.0	3136.6
76.49	24.9	76.53	3163.1	180.4	3172.5	3172.7
87.69	27.6	87.90	3197.0	214.3	3210.2	3210.1
99.12	31.1	99.55	3232.0	249.3	3249.8	3249.7
109.58	21.8	109.68	3259.6	276.9	3285.2	3285.4
120.58	25.9	120.79	3294.4	311.7	3326.1	3325.9
130.69	30.4	131.16	3327.3	344.6	3365.2	3365.1

These observations may be represented with sufficient accuracy by the expression—

$$2946.754 + 2.73502t + 0.0019463t^2 + 0.000011584t^3,$$

as the numbers in the last columns of the two tables show.

Dividing through by the first term and correcting for the expansion of the glass (0.000247), the above formula becomes:—

$$V = 1 + 0.000952845t + 0.00000683455t^2 + 0.00000003947t^3,$$

by means of which we obtain the following table; it shows the true volumes of ethene dibromide at every 5° between 0° and 135°:—

ΔC.	Volume.	Diff.	ΔC.	Volume.	Diff.
0	100000	—	75	107697	557
5	100478	478	80	108262	565
10	100960	482	85	108835	573
15	101446	486	90	109417	582
20	101936	490	95	110007	590
25	102431	495	100	110607	600
30	102931	500	105	111215	608
35	103436	505	110	111834	619
40	103946	510	115	112462	628
45	104462	516	120	113101	639
50	104984	522	125	113750	649
55	105513	529	130	114409	659
60	106049	536	135	115080	671
65	106591	542			
70	107140	549	131.45	1.14602	—

Pierre, who has already determined the expansion of this liquid, found that a single expression of the form

$$V = 1 + at + bt^2 + ct^3,$$

would not express the results of his observations with sufficient accuracy. He also selected the volume at 20.09°, the lowest temperature at which he made an observation, as the unit of volume, on the ground that at lower temperatures, particularly in the neighbourhood of its freezing point, the dilatation of the liquid might be irregular, a supposition which is not confirmed by my observations. He accordingly calculated two expressions of the form

$$V = 1 + a\theta + b\theta^2 + c\theta^3,$$

in which $\theta = t - 20.09^\circ$.

From 20.09 to 100.16° the expansion was expressed by the formula

$$V = 1 + 0.00095269619\theta + 0.000001316506858\theta^2 + 0.00000001062687\theta^3,$$

and from 100.16 to 132.6° by the formula

$$V = 1 + 0.001\,016\,765\,988\theta + 0.000\,000\,102\,231\,770\theta^2 \\ + 0.000\,000\,008\,788\,007\theta^3.$$

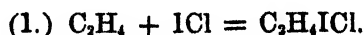
These formulæ give results differing but little from those afforded by the expression deduced from my observations, as will be evident from the following comparison:—

	20°09.	50°09.	80°09.	110°09.	130°09.
Pierre . . .	100000	102980	106213	109709	112238
Thorpe ..	100000	103003	106230	109750	112284

Ethene Chloriodide, C₂H₄ICl.

This substance was first obtained by Dr. Maxwell Simpson, who prepared it by suspending finely powdered iodine in about twice its weight of water, and passing chlorine into the liquid (which was kept cool and constantly agitated) until the iodine had nearly disappeared. After standing for a short time the yellowish-brown liquid was decanted and treated with a stream of ethene, washed by passing through soda solution, until both the liquid and the oil which separated out were decolorised. The chloriodide thus obtained boils nearly constantly after washing and drying; when first prepared it is colourless, but on exposure to light it gradually becomes red, owing to the separation of free iodine.

In order, if possible, to avoid the use of water in its preparation, I attempted to obtain the chloriodide by the direct addition of pure iodine monochloride to ethene, matters being so arranged that a large excess of the hydrocarbon was present during the reaction. The result was altogether different from what I anticipated. When the two substances are brought together, nearly the whole of the iodine is set free, and Dutch liquid is formed, only a very small quantity of the chloriodide being produced. I varied the conditions of the experiment in several ways, but with no very different result. After having spent a considerable amount of time and material in the various trials, I found that Geuther had made the same observation (*Jahrb.*, 15, 421). The reaction of ethene upon iodine monochloride appears in reality to occur in two phases: the chloriodide seems to be first formed, but under the influence of a second molecule of the iodine chloride, it is decomposed with the formation of Dutch liquid and free iodine. Thus:—



The explanation of the process employed by Dr. Maxwell Simpson would appear to be as follows:—On treating the powdered iodine sus-

pended in water with chlorine, iodine monochloride is formed, but in the outset this substance is quickly resolved into hydrochloric and iodic acids and free iodine—



In time this phase of the reaction ceases, owing partly to the decomposition of the water, and partly to the formation of hydrochloric acid, a solution of which dissolves the iodine chloride without alteration. The observations of Bornemann (*Ann. Chem. Pharm.*, 1877, 212) prove that the complete conversion of the iodine monochloride into iodic acid requires 10 parts of water to 1 part of the iodine. The extent of the decomposition would seem to depend on the ratio of the amount of the products of decomposition to the amount still undecomposed. This seems evident from the fact observed by Hannay, that if the liquid, after exhibiting no further change, be filtered from the precipitated iodine, or if that substance be removed by the addition of carbon bisulphide, further decomposition ensues, and if the iodine be constantly removed as it separates out, the whole of the monochloride is gradually but slowly decomposed in the manner indicated by the above equation. The formation of the ethene chloriodide under the conditions of Dr. Simpson's reaction is readily explained by its insolubility in water. At the moment of its formation it separates out, and is thus removed from the influence of the uncombined iodine chloride.

I am indebted to Dr. Maxwell Simpson for the sample of the chloriodide employed in my observations. After washing with dilute potash solution, and drying over phosphorus pentoxide, it boiled almost constantly between 139.1 and 140.1° . Bar., 759.3 mm., $n = 50$, $t = 30$. Corrected and reduced boiling point, 140.1° .

Two observations of specific gravity gave (1) 2.13363 at 15.28° , and (2) 2.13329 at 15.43° , compared with water at 4° . Reduced to 0° the specific gravity becomes (1) 2.16440 , and (2) 2.16437 . Mean, 2.16439 , compared with water at 4° .

Ethene chloriodide solidifies to a white crystalline mass, in a mixture of snow and hydrochloric acid.

Other observations on record are—

	Boiling point.	Specific gravity.
Simpson	$140-143^\circ$	2.151 at 0°
Maumené	146 at 753 mm.	2.39 at 20°

The following observations were made in Dilatometer C.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	8004·0	8008·6	50·66	3147·1	3147·2
12·61	3038·5	3038·4	63·56	3186·3	3186·0
25·30	3073·5	3073·9	75·82	3224·4	3224·1
37·92	3109·9	3109·9	88·23	3264·1	3263·8

In the oil-bath :—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
76·44	17·4	76·50	3213·6	219·9	3226·2	3226·2
88·51	20·4	88·77	3248·3	254·6	3265·5	3265·6
100·71	24·6	101·22	3284·6	291·0	3306·9	3307·1
114·17	28·5	114·26	3323·6	329·9	3352·6	3352·4
129·17	30·9	129·45	3368·9	375·2	3407·7	3407·7
139·66	32·7	140·16	3401·4	407·7	3448·2	3448·4

These results may be expressed by the formula—

$$3003\cdot647 + 2\cdot739\,98t + 0\cdot001\,179\,22t^2 + 0\cdot000\,013\,492t^3,$$

by means of which the numbers in the last columns of the above tables are calculated.

Dividing through by the first term, and correcting for the expansion of the glass (·0000247) we obtain—

$$V = 1 + 0\cdot000\,936\,917\,6t + 0\cdot000\,000\,415\,129t^2 + 0\cdot000\,000\,004\,501t^3,$$

which represents with sufficient accuracy the expansion of ethene chloridide between 0° and its boiling point. The following table gives the true volume of this liquid for every 5° between these limits :—

ΔC .	Volume.	Diff.	ΔC .	Volume.	Diff.
0	100000	—	85	108541	549
5	100470	470	90	109097	556
10	100942	472	95	109661	564
15	101416	474	100	110234	573
20	101894	478	105	110816	582
25	102375	481	110	111408	592
30	102860	485	115	112009	601
35	103349	489	120	112619	610
40	103843	494	125	113239	620
45	104341	498	130	113871	632
50	104845	504	135	114513	642
55	105354	509	140	115166	653
60	105868	514	145	115830	663
65	106389	521			
70	106916	527	140·1	1·15179	—
75	107450	534			
80	107992	542			

Ethene Dichloride, $C_2H_4Cl_2 = CH_2Cl.CH_2Cl$.

Prepared by the action of chlorine upon ethene. The product was washed with water, decanted, shaken with oil of vitriol, again decanted, digested with solid caustic potash, and distilled. The entire quantity boiled between 83.0 and 83.3° , the greater portion appearing to come over at 83.2° . Bar., 753.9 mm., $n = 20^\circ$, $t = 20^\circ$; corrected and reduced boiling point, 83.5° .

A determination of the specific gravity of ethene dichloride at 0° , compared with water at 4° , gave 1.28082 .

Other observers have found for the specific gravity and boiling point of this liquid:—

Regnault.....	82.5°	at 765 mm.	1.256	at 12°
Liebig.....	82.4°	—	1.247	„ 18
Pierre.....	84.92°	„ 761.88	1.28034	„ 0
Haagen.....	85°		1.2562	„ 20
Dumas.....	85°	„ 770	—	

Observations with Dilatometer C in the water-bath gave—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2947.3	2947.0	44.93	3103.8	3103.7
7.58	2972.3	2972.4	52.64	3132.5	3132.7
15.02	2997.4	2997.6	59.94	3161.0	3160.9
22.38	3022.9	3022.9	67.62	3191.7	3191.4
30.07	3049.9	3049.9	75.24	3222.6	3222.6
37.60	3076.9	3076.9	82.11	3251.2	3251.6

These observations lead to the formula—

$$2947.000 + 3.325195t + 0.002351185t^2 + 0.000028308t^3,$$

which gives the numbers in the third column of the above table.

Dividing through by the first term, and correcting for the expansion of the glass ($.0000247$), the formula becomes—

$$1 + 0.001153032t + 0.000000825693t^2 + .00000009625t^3,$$

by means of which the following table, showing the volume of ethene dichloride at every 5° between 0° and 85° , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	50	106092	648
5	100579	579	55	106752	660
10	101162	583	60	107423	671
15	101751	589	65	108108	685
20	102347	596	70	108806	698
25	102949	602	75	109518	712
30	103559	610	80	110246	728
35	104178	619	85	110989	743
40	104806	628			
45	105444	638	83.5	1.107639	—

The rate of expansion of this liquid has already been determined by Pierre (*Ann. Chim. Phys.*, [3], 19, 193) who has expressed his results by the formula—

$$1 + 0.001118932379t + 0.000001046861382t^2 + 0.000000010341738t^3.$$

which gives somewhat lower numbers than the formula calculated from my observations—

	20°.	40°.	60°.	80°.
Pierre	102288	104707	107314	110151
Thorpe	102330	104781	107399	110231

Ethidene Dichloride, $C_2H_4Cl_2 = CH_3.CHCl_2$.

This substance is now obtained in large quantities as a bye-product in the manufacture of chloral. In order to isolate it, a quantity of the partially rectified chloride, boiling between 59 and 61°, was carefully fractionated, and the portion distilling over between 60° and 60.5° (uncorr.), which was by far the largest fraction, was collected separately. Bar., 755 mm. Corrected and reduced boiling point, 59.9°.

Two determinations of specific gravity gave—

I	1.1781 at 16.63°
II	1.1779 „ 16.83°

compared with water at 4°. Reduced to 0°, these numbers become—

I	1.20388
II	1.20399
Mean	1.20394

The specific gravity and boiling point of ethidene dichloride have been frequently determined. I select the following from among the large number of recorded observations :—

	Boiling point.	Specific gravity.
Beilstein	60°	—
Krämer	60	—
Gladstone and Tribe....	61	1·201 at 13°
Darling	57—59°	1·198 „ 6·5
Geuther	59—61	1·189 „ 4·3

According to Pierre, monochlorinated ethyl chloride boils at 64·8°, under a pressure of 754·1 mm., and has a specific gravity of 1·24074 at 0°, compared with water at 4°. Regnault and also Walters observed 64°; Staedel, 62°. Both Walters and Staedel have shown, however, that it is impossible to obtain ethidene chloride free from higher chlorinated compounds by the direct action of chlorine upon ethyl chloride.

The following observations of the rate of expansion of ethidene chloride were made with Dilatometer C in the water-bath :—

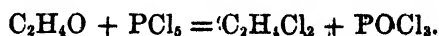
A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	3001·9	3001·8	30·84	3124·6	3124·4
5·30	3021·9	3021·9	36·84	3149·9	3149·9
10·71	3042·9	3042·9	41·94	3171·9	3172·0
15·68	3062·5	3062·5	47·88	3198·5	3198·3
20·78	3082·9	3082·9	53·81	3224·9	3225·2
25·83	3103·6	3103·6	58·67	3247·8	3247·7

These observations afford the formula—

$$3001·810 + 3·76344t + 0·0064317t^2 + 0·00001452t^3,$$

which, as the above comparison shows very accurately, represents the observed volumes.

I have made a second series of observations upon a sample of ethidene chloride, obtained by the action of phosphorus pentachloride on aldehyde :—



The product was washed with water, dried and distilled. It boiled constantly between 59·0 and 59·6° (uncorr.). Bar., 761·0° mm. Corrected and reduced boiling point, 59·2°.

Two determinations of its vapour-density, made in different tubes, gave the following results :—

	I.	II.
Weight of liquid	0·1322 gram	0·2468 gram
Volume of vapour	84·20 c.c.	115·49 c.c.
Temperature.....	100·1°	99·0°
Barometer.....	762·2 mm.	732·8 mm.
Height of column.....	393·0 „	229·4 „

	Observed.		Calculated.
	I.	II.	
Vapour-density	49·29	49·10	49·34

Two determinations of specific gravity gave—

I	1·1897 at 10·05 ^Δ
II	1·1863 „ 12·24 ^Δ

compared with water at the same temperature respectively.

These numbers reduced to 0^Δ and compared with water at 4^Δ become—

I.....	1·2050
II.....	1·2048
Mean	1·2049

Observations with Dilatometer C in the water-bath gave—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	3003·6	3003·4	33·12	3135·6	3135·6
5·36	3023·9	3023·9	37·50	3154·3	3154·2
10·59	3044·0	3044·2	42·92	3177·7	3177·7
15·88	3064·9	3065·0	48·38	3202·4	3201·9
21·43	3087·3	3087·3	53·67	3225·8	3225·9
26·73	3108·7	3108·9	56·49	3238·6	3238·8

These numbers afford the formula—

$$\text{II. } 3003\cdot400 + 3\cdot799\,05t + 0\cdot004\,734\,65t^2 + 0\cdot000\,032\,338t^3,$$

which gives the results seen in the third column of the foregoing table.

On dividing through by the first term in each of the two formula, and correcting for the expansion of the glass, we obtain—

$$\text{I. } 1 + 0\cdot001\,278\,42t + 0\cdot000\,002\,173\,58t^2 + 0\cdot000\,000\,004\,89t^3.$$

$$\text{II. } 1 + 0\cdot001\,289\,62t + 0\cdot000\,001\,607\,67t^2 + 0\cdot000\,000\,010\,806t^3.$$

These formulæ give closely accordant results, as will be evident from the following table, which shows the relative volumes of ethidene chloride at every 5^Δ between 0^Δ and 60^Δ.

Δ .	I.	II.	Mean.	Diff.
0	100000	100000	100000	—
5	100645	100649	100647	647
10	101301	101307	101304	657
15	101968	101974	101971	667
20	102648	102652	102650	679
25	103340	103341	103340	690
30	104044	104043	104044	704
35	104762	104757	104760	716
40	105493	105485	105489	729
45	106238	106227	106233	744
50	106997	106985	106991	758
55	107770	107759	107765	774
60	108559	108550	108554	789
59.9	—	—	1.08538	—
59.2	—	—	1.08426	—

The mean formula is—

$$1 + 0.00128402t + 0.00000189062t^2 + 0.00000007848t^3.$$

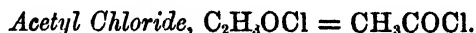
Pierre (*Ann. Chim. Phys.* [3], **31**, 118) found that the expansion of monochlorinated ethyl chloride between 0° and 61.3° may be represented by the expression—

$$1 + 0.00129071795t + 0.000000118334518t^2 + 0.000000021339432t^3,$$

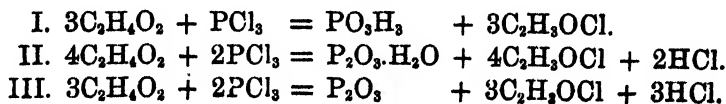
which affords very different numbers from that deduced from my observations:—

	20°.	40°.	60°.
Pierre.....	102603	105319	108249
Thorpe	102631	105460	108522

There can be little doubt that the ethidene chloride of Pierre was very far from being pure. The high specific gravity and boiling point which he observed would indicate the presence of higher chlorinated products in the material used by him: indeed, the method of preparation which he employed could hardly fail to yield a mixture of such bodies.



I prepared this liquid by the action of phosphorus trichloride upon glacial acetic acid in the manner first described by Béchamp (*Jahr.*, 1856, 427). The reaction may be represented by the following equations:—



The first equation is given in several modern text-books ; the second is that of Béchamp ; the third is identical, *mutatis mutandis*, with the reaction formulated by Gal for the mode of formation of acetyl bromide.

A mixture of 90 grams of glacial acetic acid (99 per cent.) and 69 grams of phosphorus trichloride, being the proportions demanded by Equation I, was gently heated in a flask connected with an upright condenser for several hours, and then subjected to distillation. A large quantity of hydrochloric acid gas was evolved and the acetyl chloride obtained weighed 54 grams. According to Equation I no hydrochloric acid should have been evolved, and the yield of acetyl chloride should have been 118 grams. The amount of the chloride if formed according to Equation II would be 77 grams ; and 59 grams if according to Equation III. Hence it would seem that Gal's equation correctly represents the mode in which acetyl chloride is formed by the action of phosphorus trichloride upon glacial acetic acid. The following experiments, undertaken at my suggestion by Mr. John Muir, definitely settle this point. Dehydrated acetic acid, prepared with great care, and freshly distilled phosphorus chloride were allowed to act upon each other in an apparatus so arranged that the whole of the hydrochloric acid formed in the reaction might be retained. In the first experiment—

Phosphorus trichloride.....	15·13 grams
Acetic acid	20·00 „

being the proportions required by Equation I, were mixed together. At the end of the reaction 6·03 grams of hydrochloric acid, and 13·2 grams of acetyl chloride were obtained. Equation III gives 6·04 grams hydrochloric acid gas and 12·96 grams of the chloride.

The materials were then mixed in the proportion demanded by Equation III, 6·1 grams of acetic acid being mixed with 9·3 grams of the phosphorus chloride. The amount of acetyl chloride obtained was 7·8 grams : Equation III gives 7·97 grams. In this experiment it was noticed that the two liquids when first mixed were without visible action on one another, but that when heated to about 60° the mixture became turbid, and a white precipitate was formed : on raising the temperature to about 80 or 85°, the contents of the distilling flask solidified. In all the former experiments a considerable quantity of acetic anhydride boiling between 130 and 135° was obtained. This may have been formed by the dehydrating action of the phosphorus trioxide upon the excess of acetic acid present, or by the mutual action of the acetyl chloride and acetic acid : $C_2H_3OCl + C_2H_4O_2 =$
 $\left. \begin{matrix} C_2H_3O \\ C_2H_5O \end{matrix} \right\} O + HCl.$

Kanonnikoff and Saytzeff have actually obtained the anhydride in this manner (*Ann. Chem. Pharm.*, 185, 192). The acetyl chloride obtained in the various experiments was repeatedly distilled until no further alteration in its boiling point was perceptible. Two observations made with different thermometers and at different times gave the following results :—

- I. $T = 50.25^{\circ}$ $n = 35$ $t = 17.5$ Bar. 746.1 Corr. and red. b.p. 50.90°
 II. $T = 50.43^{\circ}$ $n = 0$ $t = 0$ Bar. 746.3 „ „ 50.93°
 Mean..... 50.92° or 50.73° .

The freshly distilled product was analysed by breaking bulbs containing known quantities of the chloride in water, adding a slight excess of pure precipitated calcium carbonate, warming and determining the chlorine by decinormal silver nitrate solution and potassium chromate solution.

- I. 0.7634 gram chloride required 97.3 c.c. silver solution.
 II. 1.0009 „ „ 127.9 „ „

	Calculated.	I.	Found.	II.
Cl.....	45.20	45.20	45.31	

A determination of the specific gravity of acetyl chloride gave 1.12221 at 10.22° compared with water of the same temperature. At 0° the specific gravity becomes 1.13773 compared with water at 4° .

Other observations on record are—

- Gerhardt.... 55° boiling point 1.125 at 11°
 Kopp $55-56^{\circ}$ „ 1.1072 at 16° or 1.1305 at 0° .

Both samples were made by Gerhardt's method, i.e., by the action of phosphorus pentachloride or phosphoryl chloride upon an acetate. The last traces of the phosphoryl trichloride are removed with great difficulty, and acetic anhydride is simultaneously formed in the reaction. The difference of 4° observed in our determinations of the boiling point of acetyl chloride is doubtless due to this cause.

The following observations of the rate of expansion were made with Dilatometer E in the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2898.1	2892.8	27.46	3004.9	3005.0
4.36	2909.9	2909.9	31.32	3021.6	3021.7
9.28	2929.3	2929.5	36.02	3042.7	3042.4
13.20	2945.3	2945.4	40.34	3061.9	3061.9
18.01	2965.1	2965.1	44.72	3081.9	3082.0
22.37	2983.4	2983.3	48.20	3098.4	3098.2

These results may be represented by the formula—

$$28.92.84 + 3.895\,076t + 0.005\,909\,78t^2 + 0.000\,035\,114t^3,$$

which affords the numbers in the third column of the above table.

Dividing through by the first term and correcting for the expansion of the glass (.00002303) we obtain the formula—

$$V = 1 + 0.001\,369\,48t + 0.000\,002\,073\,9t^2 + 0.000\,000\,012\,185t^3,$$

by the aid of which the following table, showing the relative volume of acetyl chloride at every 5° between 0° and 55° is calculated:—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	35	105100	772
5	100690	690	40	105888	788
10	101391	701	45	106694	806
15	102105	714	50	107518	824
20	102832	727	55	108362	844
25	103572	740			
30	104328	756	50.73	1.07640	—

Observations on the rate of expansion of acetyl chloride have already been made by Kopp (*Ann. Chem. Pharm.*, **95**, 307), who has expressed his results by the following formula:—

$$V = 1 + 0.001\,315\,4t + 0.000\,003\,370\,6t^2,$$

which gives somewhat lower numbers than that deduced from my observations—

	15°.	30°.	45°.
Kopp.	102049	104250	106602
Thorpe	102089	104301	106661

Trichloroacetyl Chloride, $\text{CCl}_3\text{CO.Cl}$.

This liquid was obtained by the action of phosphorus trichloride on trichloroacetic acid in the manner described by Gal (*Jahr.*, 1873, 536) the trichloroacetic acid being prepared by the oxidation of chloral hydrate according to the very convenient method of Clermont (*Jahr.*, 1872, 495). The yield of the chloride obtained by Gal's method is very small, and the product even after repeated distillations persistently retains small quantities of phosphorus trichloride: that employed in the observations contained about 1.3 per cent. of the trichloride. It boiled constantly between 116.3 and 117.3°. $n = 73$, t 30°. Bar., 758 mm. Corr. and red. boiling point, 118°. This agrees with the number found by Hübner and also by Gal.

Two determinations of the sp. gr. of this liquid gave—

I	1.6305 at 15.37°
II	1.6291 „ 16.20°

compared with water at the same temperatures. Since the specific gravity of phosphorus trichloride at 0° is 1.613, the small quantity of this liquid present in the preparation could exercise but an insignificant influence on the specific gravity. The above numbers reduced to 0° and compared with water at 4° become—

I.....	1.6565
II.....	1.6563
Mean.....	1.6564

The following observations of the expansion of trichloracetyl chloride were made with Dilatometer N in the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3392.5	3392.4	52.94	3589.8	3590.3
10.75	3431.3	3431.4	64.70	3637.5	3637.4
20.80	3467.9	3468.2	73.78	3674.7	3674.9
30.96	3505.8	3505.9	84.08	3718.5	3718.9
42.08	3548.1	3548.1	99.85	3789.5	3789.7

These numbers lead to the formula—

$$3392.445 + 3.615\ 007t + 0.000\ 830\ 607t^2 + 0.000\ 028\ 114t^3,$$

by means of which the calculated volumes in the above table are obtained.

Dividing through by the first term and correcting for the expansion of the glass (0.0002553) we obtain—

$$V = 1 + 0.001\ 091\ 13t + 0.000\ 000\ 272\ 045t^2 + 0.000\ 000\ 008\ 293\ 5t^3,$$

by means of which the following table, showing the relative volumes of trichloracetyl chloride for every 5^{Δ} between 0^{Δ} and 120^{Δ} , is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	107435	611
5	100546	546	70	108056	621
10	101095	549	75	108686	630
15	101646	551	80	109328	642
20	102200	554	85	109981	653
25	102758	558	90	110645	664
30	103320	562	95	111322	677
35	103888	568	100	112013	691
40	104461	573	105	112717	704
45	105041	580	110	113436	719
50	105627	586	115	114169	733
55	106221	594	120	114918	749
60	106824	603	118	1.146168	—

Chloral, $\text{C}_2\text{Cl}_3\text{OH} = \text{CCl}_3\cdot\text{COH}$.

A quantity of this liquid, prepared from the hydrate by treatment with strong oil of vitriol and lime, was distilled. It boiled between 96° and 97.4° . It was again distilled, and the fraction which came over between 96.7° and 96.9° , which was by far the main portion, was collected separately. $n = 62$, t 28. Bar. 766.8 mm. Corrected and reduced b. p. 97.2° .

A second preparation made from another sample of chloral hydrate, after treatment with lime, boiled at 96.4° (corr. and reduced).

The specific gravity of the first sample was found to be 1.52813 at 9.43° compared with water at the same temperature. That of the second, made by a different bottle and different balance, was 1.52939 at 10.25° compared with water at 4° . These reduced to 0° , and compared with water at 4° , become respectively—

I	1.5439
II	1.5466

I am disposed to regard the first number as more nearly correct, as it was made upon a larger quantity of the liquid obtained from a much larger preparation. Giving it therefore twice the weight of the other the mean becomes 1.54480.

Other observations on record are:—

Liebig .	94°	1.502 at 18° .
Kopp ..	$98.1-99^\circ$ at 745.9	1.4903 at $22.2^\circ = 1.5183$ at 0° .

The following observations of the rate of expansion were made in the water-bath in Dilatometer E:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2879.2	2879.4	35.68	2996.5	2996.7
8.49	2906.1	2905.9	45.83	3032.4	3032.2
17.74	2936.2	2936.0	54.23	3060.9	3061.6
26.47	2965.0	2965.2	62.37	3091.1	3090.4

No observations were possible beyond 65° , owing to the appearance of gas-bubbles in the liquid.

These observations may be represented by the formula—

$$2879.369 + 3.064\ 006t + 0.008\ 000\ 75t^2 - 0.000\ 046\ 369t^3,$$

which, on dividing through by the first term and correcting for the expansion of the glass (.00002303) becomes—

$$V = 1 + 0.001\ 087\ 15t + 0.000\ 002\ 803\ 058t^2 - 0.000\ 000\ 016\ 04t^3,$$

o 2

by means of which the following table is calculated. It shows the relative volumes of chloral at every 5° between 0° and 60°:—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	35	104080	610
5	100550	550	40	104694	614
10	101114	564	45	105314	620
15	101688	574	50	105936	622
20	102274	586	55	106560	624
25	102868	594	60	107186	626
30	103470	602			

The rate of expansion of chloral has already been observed by Kopp (*Ann. Chem. Pharm.*, **95**, 307), who has expressed his results by the formula

$$V = 1 + 0.000\,954\,5t - 0.000\,002\,213\,9t^2 + 0.000\,000\,056\,939\,2t^3,$$

This gives a much slower rate of expansion than is shown by my observations, as will be evident from the following comparison:—

	20°.	40°.	60°.
Kopp	10187	10385	10615
Thorpe	10226	10462	10717

Pentachlorethane, $\text{CCl}_3.\text{CHCl}_2$.

I prepared this liquid (which was first obtained by Regnault by the prolonged action of chlorine on ethyl chloride) by the reaction discovered by Paterno (*Jahr.*, **22**, 505), viz., by the action of phosphorus pentachloride upon chloral. 190 grams of the pentachloride was added in small portions at a time to 113 grams of chloral, and the mixture boiled for some hours in a flask connected with an upright condenser. It was then distilled and all coming over below 170° was treated with water, dried by calcium chloride, and redistilled. Apparently no phosphoryl chloride was formed, as little or no liquid came over in the first distillation below 125°. The yield was much less than that indicated by the equation given by Paterno. The dehydrated liquid boiled between 157.3° and 158.8° (uncorr.), the greater portion coming over between 158.0° and 158.5°. $t\,14, n\,125$. Bar. 759.9. Corrected and reduced b. p. 159.1°.

The specific gravity was found to be 1.69263 at 10.15° compared with water at 4°. At 0° compared with water at 4° it is 1.70893.

Paterno found that pentachlorethane boils at 158°, and has a sp. gr. of 1.71 at 0° and 1.69 at 13°. The same substance obtained by Pierre by the action of chlorine on ethene dichloride boiled at 153.8° and had a sp. gr. of 1.66267 at 0° (*Jahr.*, **1**, 685).

The following observations of the rate of expansion of pentachloroethane was made in Dilatometer D. In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
6.96	3300.2	3299.8	59.66	3462.5	3462.6
14.70	3323.1	3323.3	69.59	3495.1	3494.6
31.71	3375.1	3375.3	84.65	3544.8	3544.3
48.13	3425.9	3425.2			

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
110.14	37.9	110.22	3611.6	280.7	3633.1	3633.3
117.19	43.6	117.36	3636.9	303.7	3659.1	3659.3
133.38	44.8	133.85	3689.6	358.4	3721.8	3721.7
146.32	48.2	147.19	3733.9	402.7	3775.0	3774.8

These results lead to the formula—

$$3278.618 + 3.041605t - 0.000309073t^2 + 0.0000173167t^3,$$

which on dividing through by the first term, and correcting for the expansion of the glass (.00002130) becomes—

$$V = 1 + 0.000949009t - 0.000000074503t^2 + 0.000000005280t^3,$$

by means of which the following table is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	85	108337	522
5	100474	474	90	108866	529
10	100949	475	95	109401	535
15	101424	475	100	109944	543
20	101899	475	105	110494	550
25	102376	477	110	111052	558
30	102855	479	115	111618	566
35	103335	480	120	112193	575
40	103818	483	125	112777	584
45	104304	486	130	113371	594
50	104792	488	135	113975	604
55	105285	493	140	114587	614
60	105781	496	145	115214	625
65	106282	501	150	115849	635
70	106788	506	155	116497	648
75	107298	510	160	117156	659
80	107815	517	169.1	1170079	—

Pierre found that the rate of expansion of pentachlorethane might be represented by the expressions—

$$1 + 0.000\,899\,04t + 0.000\,002\,457\,77t^2 - 0.000\,000\,012\,865t^3$$

(between 0° and 75°),

and

$$1 + 0.000\,973\,39t + 0.000\,000\,025\,77t^2 + 0.000\,000\,006\,364t^3$$

(between 75° and 148.3°).

These formulæ give a much higher rate of expansion than that deduced from my observations, as will be evident from the following comparison:—

	0°.	50°.	100°.	150°.
Pierre	100000	104949	110396	116807
Thorpe	100000	104772	109944	115874

From the close agreement of my numbers for the specific gravity and boiling point of this body with those obtained by Paterno, I am inclined to believe that Pierre's preparation, which boiled 5° lower, was mixed with less highly chlorinated products produced by the incomplete action of the chlorine on the Dutch liquid; these would tend to diminish the boiling point and specific gravity and to increase the rate of expansion.

Methene Chloride, CH₂Cl₂.

Prepared by the action of zinc-dust and ammonia upon chloroform, as described by Perkin (*Chem. News*, 18, 106). Although a considerable quantity of chloroform was worked up, but a very small yield of the chloride was obtained. This after very careful rectification through a long tube fitted with Linnemann's fractionation arrangement boiled constantly between 41 and 42°. Bar., 751.8. $n = 0$, $t = 0$. Corrected and reduced boiling point 41.6°. Butlerow, who first obtained this compound in the pure state by the action of chlorine upon methene iodide (*Ann. Chem. Pharm.*, 111, 242), found that it boiled between 40 and 41°: Perkin observed 40.4–42°.

The quantity of the liquid at my disposal was too small to enable me to determine its specific gravity by the bottle in the usual manner. The dilatometer in which the observation of the expansion was to be made was therefore weighed before and after the introduction of the chloride. The weight of the liquid taken was 4.6043 grams. This occupied—

at 11.69°	2961.7	unit-volumes,
and at 12.04	2963.1	„

Value of 1 unit-volume = 0.015578 gram of mercury at 0°.

The weight of water at 0° contained in the dilatometer at the two points would therefore be—

$$(1.) \frac{2961.7 \times 0.015578}{13.596} = 3.39334 \text{ grams.}$$

$$(2.) \frac{2963.1 \times 0.015578}{13.596} = 3.39496 \quad ,,$$

Since as the observations of the thermal expansion show 1 vol. of methene chloride at 0° occupies 1.01554 vols. at 11.69, and 1.01602 vols. at 12.04°, the specific gravity of the liquid at 0° compared with water at 4° is—

$$(1.) \frac{4.6043 \times 1.01554}{3.39334 \times 1.000129} = 1.37777$$

$$(2.) \frac{4.6043 \times 1.01602}{3.39496 \times 1.000129} = 1.37776$$

The following readings were made on Dilatometer E in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0.00	2916.0	2915.9	21.98	3002.0	3002.1
4.70	2933.7	2933.7	26.57	3021.0	3021.0
8.16	2947.0	2947.0	30.30	3036.7	3036.6
11.53	2960.1	2960.2	33.68	3051.0	3050.9
15.52	2976.1	2976.0	37.84	3068.7	3068.8
19.12	2990.4	2990.4	40.10	3078.6	3078.6

These results may be expressed by the formula—

$$2915.942 + 3.747 \, 056t + 0.007 \, 888 \, 09t^2 - 0.000 \, 004 \, 074t^3,$$

Dividing through by the first term and correcting for the expansion of the glass (0.0002303) we obtain

$$V = 1 + 0.001 \, 308 \, 05t + 0.000 \, 002 \, 735t^2 - 0.000 \, 000 \, 001 \, 33t^3,$$

by means of which the following table, showing the relative volume of methene chloride at every 5Δ between 0Δ and 45Δ, is calculated:—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	30	104167	728
5	100661	661	35	104908	741
10	101335	674	40	105662	754
15	102023	688	45	106428	767
20	102724	701			
25	103439	715	41.6	1.059052	—

Chloroform, CHCl₃.

About 500 grams of the purest commercial chloroform were frequently agitated during several days with successive quantities of water in order to remove traces of ethyl alcohol. The decanted liquid was then digested for about a week with concentrated oil of vitriol, and after separation shaken with recently heated potassium carbonate and distilled. It began to boil at 61·2°, the temperature quickly rose to 61·3°, and then slowly to 61·4°, at which point fully three-fourths of the liquid came over. Bar., 757 mm., $n = 0$, $t = 0$. Corrected and reduced boiling point, 61·20°.

Two determinations of sp. gr. at 0° gave—

I	1·52660
II	1·52653
Mean	1·52657

compared with water at 0°; compared with water at 4° the sp. gr. of chloroform at 0° is 1·52637.

Among the previous observations of the sp. gr. and boiling point of chloroform may be mentioned—

				Sp. gr.
Regnault.	61·0°			—
Pierre....	63·5	at 772·52 mm.	63·0° at 760 mm.	1·52523 at 0°.

The older determinations of Swan, Soubeiran and Mialhe, and Gregory are not given, as it does not appear that any special pains were taken to free the chloroform employed by them from accompanying alcohol.

Two series of observations of the rate of expansion were made. The following readings were taken with Dilatometer B in the water-bath :—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2896·8	2896·5	33·14	3018·5	3018·4
6·34	2918·7	2918·8	38·39	3039·0	3039·0
10·97	2935·2	2935·4	44·02	3061·5	3061·6
16·60	2955·8	2955·9	49·11	3083·2	3082·5
21·82	2975·2	2975·2	55·18	3107·5	3108·0
27·88	2996·3	2996·2	60·78	3132·0	3132·1

These numbers may be represented by the expression—

$$2896·482 + 3·490\,798t + 0·004\,856\,80t^2 + 0·000\,024\,451t^3,$$

by means of which the numbers in the third column are calculated.

The second series made with Dilatometer C gave—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3004.2	3004.1	33.15	3130.7	3130.6
6.34	3027.1	3027.2	38.39	3152.0	3151.9
10.95	3044.3	3044.4	44.01	3175.2	3175.3
16.60	3065.7	3065.7	49.10	3197.6	3197.0
21.82	3085.7	3085.7	55.17	3222.8	3222.4
27.39	3107.6	3107.5	60.78	3248.3	3248.4

numbers which may be represented by the formula—

$$3004.072 + 3.620 \, 20t + 0.005 \, 078 \, 0t^2 + 0.000 \, 024 \, 48t^3.$$

Dividing through by the first terms and correcting for the expansion of the glass, these formulæ become—

$$(I.) \, V = 1 + 0.001 \, 230 \, 7t + 0.000 \, 001 \, 707 \, 5t^2 + 0.000 \, 000 \, 008 \, 484t^3,$$

and

$$(II.) \, V = 1 + 0.001 \, 229 \, 8t + 0.000 \, 001 \, 720 \, 1t^2 + 0.000 \, 000 \, 008 \, 192t^3.$$

The mean formula is—

$$V = 1 + 0.001 \, 230 \, 24t + 0.000 \, 001 \, 713 \, 83t^2 + 0.000 \, 000 \, 008 \, 338t^3,$$

by means of which the following table, showing the relative volume of chloroform at every 5° between 0° and 65°, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	35	104551	684
5	100619	619	40	105248	697
10	101248	629	45	105959	711
15	101887	639	50	106684	725
20	102536	649	55	107424	740
25	103196	660	60	108179	755
30	103867	671	65	108950	771
			61.20	1.08362	—

According to Pierre (*Ann. Chim. Phys.* [3], 33, 199) the expansion of chloroform between 0° and 62.7° may be represented by the formula—

$$V = 1 + 0.001 \, 107 \, 15t + 0.000 \, 004 \, 664 \, 73t^2 - 0.000 \, 000 \, 017 \, 433t^3,$$

which gives a much slower rate of expansion than the formula deduced from my experiments—

	15°.	30°.	45°.	60°.
Pierre.....	101760	103694	105768	107946
Thorpe	101873	103843	105931	108152

Chloropicrin, $C(NO_2)Cl_3$.

A quantity of the pure liquid obtained by heating picric acid with bleaching powder, as directed by Hofmann (*Jahr.*, 19, 494), boiled constantly between 111.5 and 111.6° , the greater portion coming over between 111.55 and 111.58° , $n = 9^\circ$, $t = 30^\circ$. Bar., 751.9 mm. Corr. and red. boiling point = 111.91^Δ .

A determination of its specific gravity gave 1.69247 at 0^Δ compared with water at the same temperature; compared with water at 4^Δ it is 1.69225 .

Other observers have found for the boiling point of chloropicrin—

Hofmann.....	112°
Cossa	112.8° at 743 mm.

The following observations were made with Dilatometer N in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3378.8	3379.0	40.15	3529.1	3528.9
10.21	3416.2	3416.3	49.98	3567.5	3567.6
19.11	3449.4	3449.1	59.67	3606.6	3606.7
30.66	3492.5	3492.5			

In the oil-bath:—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
70.50	23.5	70.43	3638.7	247.0	3651.7	3651.4
80.31	25.4	80.38	3676.1	284.7	3694.3	3694.3
89.25	28.3	89.46	3711.7	320.3	3734.7	3734.8
102.81	30.4	103.32	3766.3	374.9	3799.4	3799.3
107.84	31.8	108.44	3786.8	395.4	3823.9	3824.1

These observations may be represented by the formula—

$$3378.99 + 3.632\ 970t + 0.001\ 480\ 70t^2 + 0.000\ 026\ 430t^3,$$

which gives the numbers in the last columns of the preceding tables.

Dividing through by the first term and correcting for the expansion of the glass ($.00002553$) this expression becomes:—

$$V = 1 + 0.001\ 100\ 7t + 0.000\ 000\ 465\ 757t^2 + 0.000\ 000\ 007\ 833t^3,$$

by the aid of which the following table, showing the relative volume of chloropicrin at every 5^Δ between 0^Δ and 110^Δ , is calculated:—

A.	Volume.	Diff.	A.	Volume.	Diff.
0	100000	—	60	106941	616
5	100552	552	65	107567	626
10	101106	554	70	108202	635
15	101664	558	75	108848	646
20	102226	562	80	109505	657
25	102793	567	85	110174	669
30	103365	572	90	110855	681
35	103943	578	95	111549	694
40	104528	585	100	112256	707
45	105119	591	105	112978	722
50	105718	599	110	113714	736
55	106325	607	111·91	1·13999	—

Carbon Tetrachloride, CCl₄.

About 300 grams of this liquid obtained by careful distillation from a large quantity of the commercially pure product, were digested with freshly heated and roughly powdered calcium chloride for a couple of days. On redistillation the liquid boiled absolutely constantly at $76\cdot47^{\circ}$, t 17° , $n = 20^{\circ}$. Bar., $754\cdot3$. Corrected and boiling point = $76\cdot74^{\circ}$.

A determination of the vapour-density of this body gave the following results:—

Weight of liquid	0·3380 gram
Volume of vapour	109·80 c.c.
Temperature	99·50
Barometer	746·9 mm.
Height of column	283·4 mm.

Found.... $76\cdot85$ Calculated.... $76\cdot73$

Two determinations of sp. gr. at 0^{Δ} gave—

- I. $1\cdot63215$
- II. $1\cdot63216$

compared with water at 0^{Δ} : compared with water at 4^{Δ} , the sp. gr. of carbon tetrachloride at 0^{Δ} is $1\cdot63195$.

Other observers have found—

	Boiling point.	Specific gravity.
Regnault	$76\cdot5$ at 760	—
Pierre	$78\cdot1$ „ $748\cdot3$	$1\cdot6298$ at 0°
Riche	$77\cdot0$?	$1\cdot567$ „ 12°
Hofmann	$77\cdot0$?	—

Two series of observations of the thermal expansion of this liquid

were made. The first set made with Dilatometer B in the water-bath gave:—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	2894·6	2894·1	41·92	3043·8	3043·7
7·00	2917·9	2918·0	48·99	3070·9	3070·8
14·14	2942·6	2942·9	55·90	3097·7	3098·0
22·15	2971·0	2971·1	62·78	3125·9	3125·9
28·26	2992·9	2993·1	69·76	3155·3	3155·0
36·19	3022·5	3022·2	76·21	3182·4	3182·8

The experimental numbers may be expressed by the formula—

$$2894\cdot08 + 3\cdot414\ 139t + 0\cdot002\ 154\ 48t^2 + 0\cdot000\ 036\ 147t^3.$$

The second series made with Dilatometer C gave the following results:—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	2989·3	2989·0	41·91	3143·7	3143·3
6·99	3013·6	3013·8	48·99	3171·5	3171·3
14·13	3039·2	3039·4	55·94	3199·0	3199·6
22·15	3068·4	3068·6	62·77	3228·4	3228·2
28·26	3091·1	3091·3	69·76	3258·6	3258·4
36·19	3121·6	3121·2	76·21	3286·7	3287·2

The observed volumes lead to the formula—

$$2988\cdot95 + 3\cdot540\ 382t + 0\cdot001\ 609\ 23t^2 + 0\cdot000\ 043\ 045t^3.$$

Dividing through by the first term, and correcting for the expansion of the glass, these formulæ become respectively—

$$\text{I. } V = 1 + 0\cdot001\ 205\ 20t + 0\cdot000\ 000\ 774\ 52t^2 + 0\cdot000\ 000\ 012\ 509t^3.$$

$$\text{II. } V = 1 + 0\cdot001\ 209\ 19t + 0\cdot000\ 000\ 567\ 65t^2 + 0\cdot000\ 000\ 014\ 448t^3.$$

The mean formula is—

$$V = 1 + 0\cdot001\ 207\ 19t + 0\cdot000\ 000\ 671\ 09t^2 + 0\cdot000\ 000\ 013\ 478t^3,$$

by the aid of which the following table, showing the relative volume of carbon tetrachloride at every 5° between 0° and 80°, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	45	105691	669
5	100605	605	50	106372	681
10	101215	610	55	107067	695
15	101830	615	60	107776	709
20	102452	622	65	108500	724
25	103081	629	70	109241	741
30	103718	637	75	110000	759
35	104365	647	80	110777	777
40	105022	657	76·74	1·10268	—

According to Pierre the expansion of carbon tetrachloride from 0 to its boiling point may be expressed by the formula—

$$V = 1 + 0\cdot001\,183\,84t + 0\cdot000\,000\,898\,881t^2 + 0\cdot000\,000\,013\,513t^3,$$

which gives very concordant results with that deduced from my observations:—

	20°.	40°.	60°.	75°.
Pierre	102414	104966	107719	109955
Thorpe	102434	104996	107750	109982

Horn represents the expansion of carbon tetrachloride between 30° and 160° by the formula—

$$V = 1 + 0\cdot001\,067\,188\,3t + 0\cdot000\,003\,565\,14t^2 - 0\cdot000\,000\,014\,942\,81t^3 + 0\cdot000\,000\,000\,085\,182\,318t^4.$$

which unquestionably fails to indicate the true rate at temperatures below the ordinary boiling point of the liquid:—

	30°	70°
Hirn	103489	108909
Thorpe	103695	109220

Bromoform, CHBr₃.

A quantity of this liquid obtained partly from Kahlbaum, of Berlin, and partly from Schuchardt, of Görlitz, was distilled, digested with calcium chloride, and again distilled. The liquid boiled constantly between 149·2 and 150·0°, the greater portion coming over between 149·6 and 149·7°. $t = 21^\circ$, $n = 120$. Bar., 761·6 mm. Corr. and red. b. p. = 151·2°.

Bromoform solidifies at 2·5° in lustrous crystalline plates—a fact apparently hitherto unnoticed.

A determination of the specific gravity of bromoform gave 2·81185 at 8·56° compared with water at the same temperature: its sp. gr. at 0° (on the assumption that it remained liquid at that temperature, and contracted regularly) would be 2·83413, compared with water at 4°.

Other observers have found for the specific gravity and boiling point of bromoform :—

Cahours.....	152° ? Bar.	2·9 at 12°
Lowig	—	2·13 ?
Schmidt	149—150	2·775 at 14·5°
Bolas and Groves ...	144—146	—

The following observations were made with Dilatometer D in the water-bath :—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
12·50	3287·1	3287·6	45·70	3390·2	3389·7
25·51	3327·1	3327·1	62·31	3442·8	3442·9
35·92	3359·5	3359·2			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
74·25	22·6	74·23	3475·1	137·0	3482·0	3482·2
87·61	27·3	87·79	3517·8	179·7	3528·5	3528·3
98·50	31·2	98·87	3553·1	214·9	3567·4	3567·2
115·45	29·1	115·62	3604·7	266·5	3627·9	3628·3
124·38	32·3	124·65	3634·8	296·7	3662·8	3662·5
139·73	36·1	140·30	3686·4	348·2	3724·2	3724·2
145·71	38·6	146·49	3707·2	369·1	3749·2	3749·5

These results lead to the formula—

$$3250\cdot042 + 2\cdot989\ 60t + 0\cdot000\ 839\ 85t^2 + 0\cdot000\ 013\ 826t^3,$$

from which, on dividing through by the first term and correcting for the expansion of the glass, we obtain—

$$V = 1 + 0\cdot000\ 941\ 16t + 0\cdot000\ 000\ 278\ 00t^2 + 0\cdot000\ 000\ 004\ 259t^3,$$

by means of which the numbers in the following table, showing the relative volumes of bromoform at every 5° between 0° and 150°, are calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	85	108462	537
5	100471	471	90	109006	544
10	100944	473	95	109557	551
15	101419	475	100	110116	559
20	101897	478	105	110682	566
25	102376	479	110	111256	574
30	102868	482	115	111839	583
35	103346	488	120	112430	591
40	103837	491	125	113031	601
45	104331	494	130	113641	610
50	104829	498	135	114260	619
55	105331	502	140	114890	630
60	105839	508	145	115530	640
65	106351	512	150	116180	650
70	106870	519			
75	107395	525	151.2	1.16338	—
80	107925	530			

Trichlorobrommethane, CCl₃Br.

This compound was prepared according to the method by which it was first obtained by Paterno, viz., by the action of bromine upon chloroform.



The materials were heated together in sealed tubes for several days to a temperature of about 210°, the tubes being occasionally opened to allow of the escape of the hydrobromic acid gas. On each occasion the liquid was distilled, and all coming over below 95° was reheated. The distilled product, containing a slight excess of bromine, was treated with an aqueous solution of potash and dried over calcium chloride. On fractionation by far the greater portion of the liquid boiled between 102 and 103°; $n = 100^\circ$; $t = 18^\circ$. Bar., 755.5 mm. Corrected and reduced boiling point = 104.07°.

Trichlorobrommethane, when freshly prepared, is a colourless liquid possessing a pleasant aromatic smell; on exposure to light it gradually becomes brown owing to the liberation of a small quantity of bromine.

Two determinations of its specific gravity gave—

2.03674 at 8.41°

2.03492 „ 9.31°

compared with water at the same temperature. These numbers give for the specific gravity at 0° compared with water at 4°—

I 2.05494

II 2.05498

Mean 2.05496

Paterno found the boiling point of this compound to be 104.3° , and its specific gravity at 0° (compared with water at the same temperature ?) to be 2.058. These numbers agree closely with those of my own determinations. Friedel and Silva (*Jahr.*, 1872, 300) found $103-104^{\circ}$ at 752 mm.; sp. gr. 2.063 at 0° , and 2.016 at 25° .

The following observations of the rate of expansion were made with Dilatometer N in the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3429.3	3428.9	46.82	3605.2	3605.2
9.57	3463.6	3463.8	56.21	3642.6	3642.9
18.34	3496.0	3496.2	65.69	3682.2	3681.9
27.97	3532.3	3532.4	75.08	3721.7	3721.6
35.15	3560.0	3559.8			

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
81.64	21.2	81.76	3726.4	340.5	3750.2	3750.5
90.73	22.9	90.99	3761.8	375.9	3791.7	3791.5
101.35	24.5	101.89	3803.4	417.6	3841.9	3841.7

These observations may be represented by the formula—

$$3428.89 + 3.623\,57t + 0.002\,156\,213t^2 + 0.000\,020\,032t^3,$$

which affords the numbers in the last columns of the above tables.

Dividing through by the first term and correcting for the expansion of the glass (0.0002553), this formula becomes—

$$V = 1 + 0.001\,082\,31t + 0.000\,000\,655\,82t^2 + 0.000\,000\,005\,858\,2t^3,$$

by the aid of which the following table, showing the volume of trichlorobrommethane at every 5^{Δ} between 0^{Δ} and 105^{Δ} , is calculated.

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	60	106857	608
5	100543	543	65	107473	616
10	101089	546	70	108098	625
15	101640	551	75	108733	635
20	102196	556	80	109378	645
25	102756	560	85	110033	655
30	103322	566	90	110699	666
35	103894	572	95	111376	677
40	104472	578	100	112065	689
45	105057	585	105	112766	701
50	105649	592			
55	106249	600	104.07	1.12634	—

Propionitrile, C₃H₅.CN.

About 200 grams of this liquid, obtained from Kahlbaum, of Berlin, was treated with dilute hydrochloric acid, dried and distilled, and the portion boiling between 96·4 and 96·6° (uncorr.) was collected separately: it formed fully nineteen-twentieths of the whole quantity; $n = 37\cdot5$; $t = 12\cdot0$. Bar., 751·6 mm. Corrected and reduced boiling point, 97·08°.

That the liquid was pure will be evident from the following determination of its vapour-density:—

Weight of liquid	0·0512 gram
Volume of vapour	80·78 c.c.
Temperature	99·6°
Barometer	749·1 mm.
Mercury column	482·0 „

Found 27·48 Calculated 27·46

Its specific gravity was found to be 0·79375 at 7·36° compared with water at 4°: at 0°, compared with water at 4°, it is 0·80101.

Other observations on record are—

Limpricht	97—98°
Gautier	96·7°
Engler	98·1° (from barium sulphovinate and potassium cyanide)
„	97·6—98·0° (by action of phosphorus pentoxide on propionamide).

The older determinations are not given, as they were evidently made upon impure material, contaminated probably with the isomeric ethyl carbamine. No determination of the specific gravity of the pure substance seems to have been hitherto made.

The following observations of the expansion by heat were made in Dilatometer N in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	3394·4	3395·0	53·01	3632·8	3632·9
10·52	3439·0	3438·8	61·93	3677·5	3677·7
19·57	3478·1	3477·7	73·22	3736·8	3736·7
27·24	3511·9	3511·6	80·55	3776·1	3776·3
35·85	3550·3	3550·8	91·50	3837·5	3837·7
43·99	3589·1	3589·2			

These observations may be represented by the formula—

$3395.037 + 4.082\ 285t + 0.006\ 824\ 85t^2 + 0.000\ 015\ 700t^3$,
which affords the numbers in the third column of the above table.

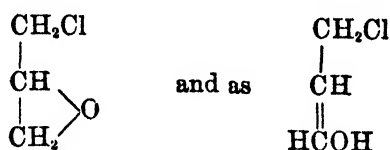
Dividing through by the first term, and correcting for the expansion of the glass ($\cdot 00002553$), this expression becomes—

$V = 1 + 0.001\ 227\ 75t + 0.000\ 002\ 040\ 64t^2 + 0.000\ 000\ 004\ 675t^3$,
which affords the following table, showing the relative volumes of propionitrile at every 5^Δ between 0^Δ and 100^Δ .

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	60	108202	754
5	100619	619	65	108971	769
10	101249	630	70	109755	784
15	101889	640	75	110553	798
20	102541	652	80	111367	814
25	103204	663	85	112197	830
30	103879	675	90	113044	847
35	104567	688	95	113906	862
40	105267	700	100	114786	880
45	105981	714			
50	106707	726	97.08	1.142699	—
55	107448	741			



The constitution of epichlorhydrin has been variously represented as—



In the former expression it is seen that the oxygen is directly connected with two of the carbon atoms; whereas in the latter it is present as hydroxyl. The experiments of Darmstädter leave, however, very little doubt that the first formula correctly represents the structure of this compound. As a knowledge of the specific volume of epichlorhydrin would probably serve to throw additional light on the matter, I have prepared a quantity of this liquid, and have determined its boiling point, specific gravity, and thermal expansion.

A large quantity of dichlorhydrin was first prepared by Berthelot's method as modified by Reboul (*Jahr.*, 12, 456), and this was converted into epichlorhydrin by treatment with potash. The epichlorhydrin boiled constantly between 116.75 and 117.00° , the greater portion coming over at 116.9° . $n = 10$; $t\ 19^\circ$. Bar., 762.2 mm. Corrected and reduced boiling point 116.56^Δ .

Two determinations of specific gravity gave—

I.....	1.19108 at 10.15 ^A
II.....	1.18783 „ 13.07 ^A

compared with water at the same temperature. Reduced to 0^A, and compared with water at 4^A, these numbers became—

I.....	1.20316
II.....	1.20310
Mean.....	1.20313

Other observations on record are—

Darmstädter.....	117° at 755.5	1.204 at 0°
Reboul.....	118—119°	1.194 „ 11°.

The following observations were made with Dilatometer N in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0.00	3379.8	3380.3	42.06	3528.1	3527.9
11.12	3418.2	3418.3	55.77	3578.9	3579.2
20.93	3452.8	3452.3	64.07	3611.7	3611.3
31.94	3491.3	3491.2			

In the oil-bath:—

T°.	t.	T ^A .	V.	E.	Observed.	Calculated.
64.13	20.9	64.01	3602.3	189.2	3611.0	3611.1
73.85	24.0	70.83	3638.1	224.9	3650.2	3650.1
83.83	28.8	83.95	3675.7	262.5	3691.6	3691.9
96.24	31.2	96.58	3723.6	310.5	3746.7	3746.2
105.80	34.7	106.33	3761.1	348.0	3789.9	3789.9
114.87	25.9	115.04	3790.8	377.7	3830.0	3830.5

These results may be expressed by the formula—

$$3380.336 + 3.384\ 624t + 0.002\ 009\ 22t^2 + 0.000\ 022\ 445\ t^3.$$

Dividing through by the first term, and correcting for the expansion of the glass (.00002533), this expression becomes—

$$V = 1 + 0.001\ 026\ 60t + 0.000\ 000\ 619\ 74t^2 + 0.000\ 000\ 006\ 657t^3,$$

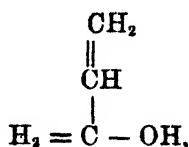
by means of which the following table, showing the relative volume of epichlorhydrin at every 5^A between 0^A and 120^A, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	107118	592
5	100515	515	70	107718	601
10	101033	518	75	108329	610
15	101556	523	80	108950	621
20	102083	527	85	109583	633
25	102616	533	90	110227	644
30	103154	538	95	110883	656
35	103698	544	100	111551	668
40	104248	550	105	112233	682
45	104806	558	110	112929	696
50	105371	565	115	113638	709
55	105944	573	120	114362	724
60	106526	582	116.55	1.18861	—

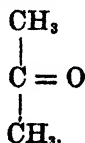
Allyl Alcohol, $C_3H_5OH = CH_2CHCH_2OH$.

On the publication of Tollens and Henninger's memoir, "On the Preparation of Allyl Alcohol" (*Ann. Chem. Pharm.*, 156, 134), Kopp remarked in a note appended to the paper that a comparison of the specific volume of the alcohol with that of its isomeride acetone would doubtless throw light on the relation of the specific volume of a body to its molecular structure.

It is definitely established that allyl alcohol, made from glycerin and oxalic acid or obtained by the action of sodium on dichlorhydrin, has the constitution—



whereas the constitution of acetone or dimethylketone is—



Adopting Kopp's values, the calculated specific volumes of these liquids are—

Allyl alcohol	73.8
Acetone.....	78.2

the difference being, of course, due to the variation in the mode of combination of the oxygen (see p. 142).

Tollens determined the rate of expansion of allyl alcohol by estimating its specific gravity at different temperatures by means of the

pyknometer, and he found that its volume at t° might be expressed with approximate accuracy by the formula—

$$V = 1 + 0.000879t + 0.0000026t^2,$$

the volume at 0° being 1. The boiling point of the allyl alcohol was 97° , and its specific gravity at 0° , compared with water at the same temperature, was 0.8709. Hence its specific gravity at the boiling point was $\frac{0.8709}{1.10973} = 0.7848$ and its specific volume $\frac{58}{0.7848} = 73.90$, agreeing almost exactly with the calculated value.

The accuracy of this determination of the specific volume of allyl alcohol was called in question by H. L. Buff. Buff was of opinion that the specific volume of carbon in combination is not invariable, as Kopp supposes, and he found experimental evidence to support this proposition in the relatively high specific volumes of certain allyl derivatives, notably of diallyl, in which, moreover, he assumed the existence of dyad carbon. In fact, Buff concluded that the specific volume of an element was a function of, or was related to, its combining value, and as he assumed that carbon had a variable combining value, he assumed too that it had a variable specific volume. Buff was led to redetermine the specific volume of allyl alcohol, and in a preliminary note published in the *Ber.* for July, 1876, he states that he had actually found the value to be considerably higher than the calculated number in accordance with his hypothesis. The number he gives, viz., 74.6, was regarded by him as provisional and probably too low, as he was of opinion that the alcohol which served for his experiments was incompletely dehydrated: his expressed intention to repeat the determination on a larger quantity of the anhydrous alcohol was frustrated by his death in the following year.

As the question was still open, I suggested to Mr. James Monckmann, a former student in the laboratory of the Yorkshire College, that he should prepare a quantity of allyl alcohol by Tollens's method from glycerin and oxalic acid with a view of determining its specific gravity and thermal expansion. About $\frac{1}{2}$ kilo. of the alcohol was boiled for some hours with caustic soda, distilled and digested for about a fortnight with a concentrated aqueous solution of acid sodium sulphite to remove any admixed acrolein. After separating the sulphite solution the alcohol was treated with recently ignited potassium carbonate and repeatedly digested with quicklime (the alcohol being distilled off the lime after each digestion) until its specific gravity was constant.

The last four determinations of specific gravity were—

I.....	0.8574	
II.....	0.8575	Temp. 15°.
III.....	0.8573	
IV.....	0.8573	

The mean is 0.85738 at 15° compared with water at the same temperature. This number agrees exactly with that of Dittmar and Steuart (*Proc. Phil. Soc.*, Glasgow, 1875-76, 64), viz., 0.8576 at 15° compared with water at 15.5. Tollens found (1) 0.8709 at 0°, and (2) 0.86045 at 13°, compared with water at 0°; from his interpolation formula the specific gravity at 15°, compared with water at 15°, would be (1) 0.8597, and (2) 0.8594. Allyl alcohol retains traces of water with extraordinary tenacity, a fact already noticed by Tollens and Dittmar. Repeated and prolonged treatment with freshly heated quicklime is required to dehydrate it completely. Altogether our alcohol stood for 38 days over six successive quantities of lime before its specific gravity became constant. As the dehydration proceeded we noticed the remarkable rise in the boiling point observed by Dittmar and Steuart. After the first treatment with lime the alcohol boiled at 92°, after the third it boiled at 94.5°, and finally boiled constantly between 95.9° and 96.3°, the greater portion coming over between 96.0° and 96.3. $n = 51$, $t = 18.5^\circ$. Barometer 0.766 mm. Corrected and reduced boiling point 96.6°.

* A determination of the vapour-density afforded the following data:—

Weight of liquid	0.0954 gram
Volume of vapour.....	93.0 c.c.
Temperature	99.8°
Barometer	753 mm.
Height of column.....	413 "

Found.... 28.85

Calculated.... 28.93

The following observations of the rate of expansion were made with Dilatometer C in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0.00	3022.9	3022.5	34.67	3130.5	3130.4
9.44	3050.9	3051.1	43.25	3158.8	3158.8
17.25	3074.9	3075.1	51.86	3187.9	3188.3
26.06	3102.7	3102.7	60.47	3218.9	3219.0

In the oil-bath :—

T°.	t°.	T ^Δ .	V.	E.	Observed.	Calculated.
69·52	29·1	69·46	3241·1	257·5	3252·9	3252·3
79·38	30·0	79·43	3274·5	290·8	3290·9	3291·1
84·58	30·8	84·74	3293·4	309·7	3312·8	3312·7
93·24	30·1	93·55	3324·2	340·5	3349·9	3349·8

These results may be expressed by the formula—

$$3022·531 + 3·003\ 52t + 0·001\ 813\ 10t^2 + 0·000\ 037\ 132t^3.$$

On dividing through by the first term and correcting for the expansion of the glass (·0000247), we obtain—

$$V = 1 + 0·000\ 993\ 71t + 0·000\ 000\ 599\ 861t^2 + 0·000\ 000\ 012\ 285t^3,$$

by means of which the following table, showing the relative volume of allyl alcohol at every 5^Δ between 0^Δ and 100^Δ, is calculated :—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	55	105995	593
5	100511	511	60	106601	606
10	101026	515	65	107222	621
15	101546	520	70	107857	635
20	102072	526	75	108508	651
25	102604	532	80	109176	668
30	103145	541	85	109863	687
35	103694	549	90	110568	705
40	104252	558	95	111293	725
45	104821	569	100	112038	745
50	105402	581	96·6	111529	—

The above observations show that allyl alcohol is considerably more expansible than Tollens's formula would indicate—

	20°.	40°.	60°.	80°.	96·6°.
Tollens.....	101862	103932	106210	108696	110916
Thorpe.....	102058	104230	106579	109163	111529

The specific gravity of allyl alcohol at 0° compared with water at 0° is 0·87063; compared with water at 4^Δ it is 0·8699; at 96·6^Δ it is 0·7800; hence its specific volume is $\frac{57·87}{0·7800} = 74·19$.

The volume thus obtained agrees so nearly with that calculated by means of Kopp's values that we must conclude that allyl alcohol fails to afford any evidence that the specific volume of carbon is variable.

Acetone, $C_3H_6O = CH_3.CO.CH_3$.

A quantity of this liquid obtained from Kahlbaum, in Berlin, was purified by converting it into the acid sodium sulphite compound. It boiled absolutely constantly between 55.78 and 55.80° . $n = 0$, $t' = 0$. Barometer 728.2 mm. Corrected and reduced boiling point 56.53° .

A determination of vapour-density gave the following numbers:—

Weight of liquid.....	0.0735 gram.
Volume of vapour	61.6 c.c.
Temperature	99.4°
Barometer	742.5 mm.
Height of column	487.0 „
Found....	28.35
Calculated....	28.93

Two determinations of specific gravity gave—

- I. 0.80755 at 10.22°
 II. 0.80636 at 11.27°

compared with water at the same temperature. Reducing these results by means of the formula given on p. 213, they give for the specific gravity at 0° —

- I. 0.81858
 II. 0.81858

compared with water at 4° .

Other observations on record are—

Liebig.....	0.7921 at 18.0°	0.811 at 0°
Kopp	0.79045 „ 13.9	0.8143 „
Linnemann....	0.7938 „ 18.0	0.8127 „
„	0.7975 „ 15.0	0.8134 „

Kopp found the boiling point of acetone to be 56.3° at 763 mm., which agrees exactly with Regnault's number derived from vapour-tension observations.

A series of observations made with Dilatometer C in the water-bath afforded the following numbers:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3046.8	3046.6	29.60	3174.1	3174.4
4.98	3066.9	3067.0	34.71	3198.3	3198.0
9.71	3086.7	3086.8	39.94	3222.7	3222.7
14.95	3109.2	3109.1	44.63	3245.2	3245.1
19.72	3130.1	3130.0	49.39	3268.7	3268.6
24.67	3151.8	3152.0	54.79	3295.5	3295.5

These numbers afford the formula—

$$3046.624 + 4.046\,628t + 0.009\,116\,88t^2 - 0.000\,001\,113t^3,$$

which gives the results contained in the third column of the above table.

Dividing through by the first term and correcting for the expansion of the glass (·0000247), we obtain—

$$V = 1 + 0.001\,352\,93t + 0.000\,003\,024\,26t^2 - 0.000\,000\,000\,29t^3,$$

which gives the following table showing the relative volume of acetone at every 5° between 0° and 60°.

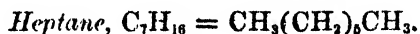
Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	35	105104	774
5	100684	684	40	105894	790
10	101383	699	45	106698	804
15	102097	714	50	107517	819
20	102827	730	55	108351	834
25	103571	744	60	109200	849
30	104330	759	56.53	1.086092	—

The rate of expansion of acetone has already been determined by Kopp (*Pogg. Ann.*, **72**, 1 and 223), who found that it might be expressed by the formula—

$$V = 1 + 0.001\,348\,1t + 0.000\,002\,609t^2 + 0.000\,000\,011\,559\,2t^3,$$

which gives results in close agreement with that deduced from my observations, as the following comparison shows:—

	15°.	30°.	45°.
Kopp	102085	104310	106700
Thorpe	102082	104303	106666



I made several trials to procure this body in a state of sufficient purity to warrant the attempt to determine its rate of thermal expansion by the fractional distillation of so-called "cracked" paraffin oil, but the results were not very satisfactory. No two samples of the hydrocarbon, although boiling at approximately constant and almost identical temperatures, had the same specific gravity or the same rate of expansion. My friend Schorlemmer sent me from time to time various specimens of heptane separated with all possible care from petroleum, but the specific gravities and rates of expansion of these products were equally discordant, and I came to the conclusion that it was impossible to separate the pure hydrocarbon from its congeners by the ordinary processes of fractional distillation.

The discovery that the exudation from the nut-pine or Digger pine

(*Pinus sabiniana*), a tree indigenous to California, constitutes an abundant source of almost absolutely pure heptane, has enabled me to obtain a more satisfactory result, and it is with this vegetable heptane that all the determinations herein given have been made. For details of the mode of separation and purification of the hydrocarbon I may refer to my paper "On Heptane from *Pinus sabiniana*" (*Chem. Soc. J.*, June, 1879).

The heptane boiled absolutely constantly. The first observation gave 98.27° at 755.6 mm.; the second 97.97° at 746.9 mm.; column in both cases entirely immersed. Corrected and reduced boiling points 98.42° and 98.43° .

Two determinations of vapour-density gave—

	I.	II.
Weight of liquid....	0.1445 gram	0.0769 gram
Volume of vapour ..	90.39 c.c.	69.77 c.c.
Temperature	99.90°	99.60°
Barometer	757.6 mm.	749.0 mm.
Height of column ..	387.8 "	493.4 "

	Found.
Calculated.	I. II.
49.90	50.07 49.94

Three determinations of specific gravity made with different bottles gave the following results:—

I.....	0.68848 at 14.98°
II.....	0.68855 at 14.87°
III.....	0.68859 at 14.87°

compared with water at the same temperature. Reducing these numbers by the formula given below, the specific gravity at 0° compared with water at 4° becomes—

I.....	0.70048
II.....	0.70046
III.....	0.70049
Mean.....	0.70048

Two series of determinations of the rate of expansion were made. The first in Dilatometer D gave the following data:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	3290.1	3290.4	53.71	3516.3	3516.9
9.04	3326.1	3326.0	62.80	3560.1	3559.9
17.27	3359.2	3359.1	72.12	3606.2	3605.7
26.96	3398.9	3399.1	80.68	3649.5	3649.5
35.55	3435.9	3435.7	87.32	3684.2	3684.6
44.96	3477.2	3477.1	93.70	3719.9	3719.4

These results lead to the formula—

$$3290.361 + 3.895\,352t + 0.004\,320\,87t^2 + 0.000\,031\,83t^3.$$

The second series made in Dilatometer E afforded the following numbers :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2879.6	2879.3	53.71	3076.4	3077.0
9.04	2910.5	2910.6	62.81	3114.5	3114.5
17.27	2939.3	2939.5	72.13	3155.2	3154.7
26.97	2974.2	2974.5	80.68	3193.6	3193.2
35.54	3006.4	3006.2	87.27	3223.8	3224.1
44.96	3042.3	3042.3	93.71	3255.3	3255.4

From these numbers we obtain the expression—

$$2879.302 + 3.432\,882t + 0.002\,478\,31t^2 + 0.000\,039\,64t^3,$$

by means of which the numbers in the third column of the foregoing table are calculated.

Dividing through by the first terms, and correcting for the expansion of the glass of the dilatometers (0.0000213 and 0.00002303), the formulæ become respectively—

$$\text{I. } V = 1 + 0.001\,205\,17t + 0.000\,001\,338\,41t^2 + 0.000\,000\,099\,701t^3,$$

and

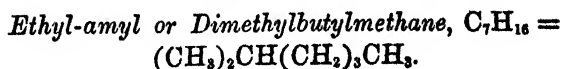
$$\text{II. } V = 1 + 0.001\,215\,29t + 0.000\,000\,888\,19t^2 + 0.000\,000\,013\,787t^3.$$

The mean formula is—

$$V = 1 + 0.001\,210\,23t + 0.000\,001\,113\,3t^2 + 0.000\,000\,011\,74t^3,$$

by the aid of which the following table, showing the relative volume of heptane at every 5^Δ between 0^Δ and 100^Δ , is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	55	107188	712
5	100608	608	60	107916	728
10	101222	614	65	108659	743
15	101844	622	70	109420	761
20	102474	630	75	110198	778
25	103114	640	80	110995	797
30	103763	649	85	111812	817
35	104423	660	90	112650	838
40	105094	671	95	113509	859
45	105778	684	100	114390	881
50	106476	698	98.43	1.14111	—



I am indebted to Mr. Harry Grimshaw for the sample of this hydrocarbon which served for my observations. It was obtained by the action of sodium on a mixture of the bromides of ethyl and amyl, and was purified with very great care. For its analysis see *Chem. Soc. J.*, 1873, 300. It boiled constantly between 90.5° and 91° under a pressure of 762.3 mm. Corrected and reduced boiling point 90.3° .

Two determinations of its specific gravity at 0° afforded the following results:—

I.	0.69631
II.	0.69692

compared with water at 4° . Grimshaw found that ethyl-amyl boils at 90° , and that its specific gravity was 0.6833 at 18.4° compared with water at the same temperature. This at 0° and reduced to a vacuum becomes 0.6990 compared with water at 4° .

Two series of observations of the rate of expansion were made. The first in Dilatometer B gave the following numbers:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2868.7	2868.1	53.95	3071.4	3071.5
9.12	2899.9	2900.2	62.63	3108.6	3108.6
17.84	2931.4	2931.6	71.62	3148.8	3148.5
26.73	2964.1	2964.4	80.94	3191.6	3191.9
35.75	2998.8	2998.6	86.63	3219.6	3219.6
44.72	3033.9	3033.8			

These results may be expressed by the formula—

$$2868.122 + 3.49539t + 0.00280228t^2 + 0.000042541t^3.$$

The second series made with Dilatometer C gave the following results:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2967.7	2967.4	53.97	3177.8	3178.1
9.12	3000.3	3000.5	62.63	3216.3	3216.2
17.84	3033.0	3033.0	71.63	3257.6	3257.4
26.74	3066.7	3066.9	80.93	3301.6	3301.9
35.76	3102.6	3102.5	86.63	3330.2	3330.2
44.71	3139.0	3139.0			

These numbers lead to the formula—

$$2967.443 + 3.590505t + 0.00400119t^2 + 0.0000333096t^3,$$

which gives the numbers in the third column of the above table.

Dividing through by the first terms respectively and correcting for the expansion of the glass we obtain—

I. $V = 1 + 0.0012442t + 0.00000100812t^2 + 0.000000014857t^3$,
and

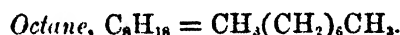
II. $V = 1 + 0.0012347t + 0.00000137825t^2 + 0.000000011258t^3$.

The mean formula is—

$$V = 1 + 0.0012394t + 0.00000119318t^2 + 0.000000013058t^3,$$

by means of which the following table, showing the relative volume of ethyl-amyl at every 5° between 0° and 95° , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	55	107395	736
5	100623	623	60	108148	753
10	101253	630	65	108919	771
15	101890	637	70	109709	790
20	102537	647	75	110518	809
25	103194	657	80	111348	830
30	103861	667	85	112199	851
35	104540	679	90	113070	871
40	105232	692	95	113963	893
45	105938	706	90.3	1.131264	—
50	106659	721			



I am indebted to Professor Schorlemmer for the sample of this liquid which has served for my observations. It was obtained from methyl-hexyl-carbinol, and after rectification over sodium boiled between 125.3 and 126.8° . $n = 23$, $t = 19$. Bar., 760.8 mm. Corrected and reduced boiling point = 125.46° .

A determination of vapour-density afforded the following numbers:—

Weight of liquid..... 0.0786 gram

Volume of vapour 65.33 c.c.

Temperature 99.3°

Barometer 740.2 mm.

Height of column 503.3 „

Found 56.68

Calculated 56.88

Two determinations of specific gravity at 0° gave the following results:—

I..... 0.71882

II..... 0.71885

Mean..... 0.71883

compared with water at 4° .

The following observations of the rate of expansion of octane were made with Dilatometer D.

In the water-bath :—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
18·32	3248·6	3248·6	42·03	3340·2	3339·7
20·95	3258·5	3258·5	55·77	3394·7	3395·3
32·02	3300·3	3300·7	63·86	3429·4	3429·3

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
64·07	20·7	63·95	3424·6	96·4	3429·7	3429·7
73·87	24·2	73·85	3464·3	136·2	3472·8	3472·7
83·69	28·7	83·81	3505·3	177·2	3517·8	3518·0
96·19	31·4	96·52	3559·6	231·4	3579·4	3578·9
106·26	34·6	106·75	3603·7	275·6	3630·6	3630·9

These results may be expressed by the formula—

$$3180.483 + 3.69492t + 0.00051493t^2 + 0.000041167t^3,$$

which gives the numbers contained in the last columns of the above tables.

Dividing through by the first term and correcting for the expansion of the glass (·0000213) we obtain the following expression, as representing the expansion of octane between 0° and its boiling point.

$$V = 1 + 0.00118304t + 0.000000186648t^2 + 0.00000012947t^3,$$

by means of which the following table, showing the relative volume of octane at every 5° between 0° and 125°, is calculated :—

A.	Volume.	Diff.	A.	Volume.	Diff.
0	100000	—	65	108124	679
5	100592	592	70	108817	683
10	101186	594	75	109524	703
15	101783	597	80	110247	723
20	102384	601	85	110986	739
25	102990	606	90	111742	756
30	103601	611	95	112518	776
35	104219	618	100	113312	794
40	104845	626	105	114127	815
45	105479	634	110	114963	836
50	106124	645	115	115821	858
55	106779	655	120	116702	881
60	107445	666	125	117606	904
			125·46	1·17693	—



Prepared by Mr. W. C. Williams, of the Owens College, Manchester, by the action of sodium on isobutyl iodide. The hydrocarbon thus obtained was treated with a mixture of concentrated sulphuric and nitric acids, washed with water, dried by potash, and distilled over sodium. It boiled between $108\cdot2$ and $108\cdot7^\circ$. $n_D = 0$. Bar., $748\cdot2$ mm. Corrected and reduced boiling point = $108\cdot53^\circ$.

Williams observed $108-108\cdot3^\circ$ at 745 mm. on the same preparation (*Chem. Soc. J.*, March, 1879). That the hydrocarbon was of a high degree of purity will be evident from the following determination of vapour-density:—

Weight of liquid	0·1449 gram
Volume of vapour	85·30 c.c.
Temperature	$99\cdot1^\circ$
Barometer	$734\cdot9$ mm.
Height of mercury	$389\cdot7$ „
Found	$56\cdot90$
Calculated	$56\cdot88$

Two determinations of specific gravity at 0° compared with water at 4° gave—

I	0·71109
II	0·71111
Mean	0·71110

Other observers have found—

Kolbe.....	108	?	$0\cdot694$	at 18°
Kopp.....	$108\cdot5$	at $747\cdot5$ mm.	$0\cdot7135$	„ 0
Wurtz	106	?	$0\cdot7057$	„ 0
Williams ..	$108\cdot2$	„ 745 mm.	$0\cdot7085$	„ 0
„ ..	$108-108\cdot3$	at 745 mm.	$0\cdot7091$	„ 0

The following observations of the rate of expansion were made in Dilatometer E.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2887·1	2887·0	39·07	3024·4	3024·5
9·70	2919·9	2920·1	48·24	3059·2	3059·1
19·60	2954·1	2954·4	59·68	3103·8	3104·0
29·19	2988·3	2988·4	68·86	3143·9	3141·8

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
69·47	23·3	69·39	3129·6	241·5	3144·1	3144·1
78·92	26·0	79·06	3166·4	278·3	3185·9	3185·9
89·99	29·5	90·21	3210·4	322·3	3237·2	3236·7
97·80	31·6	98·19	3242·5	354·3	3275·4	3275·4
106·79	30·7	107·39	3278·0	389·9	3320·7	3320·6

These results lead to the expression—

$$2886.980 + 3.38927t + 0.0017154t^2 + 0.00004085t^3,$$

by means of which the numbers in the last columns of the above tables are calculated.

Dividing through by the first term and correcting for the expansion of the glass (·00002303) the above formula becomes—

$$V = 1 + 0.00119701t + 0.000000621221t^2 + 0.00000014166t^3,$$

by the aid of which the following table, showing the relative volume of di-isobutyl at every 5° between 0° and 108·53°, is calculated.

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	60	107712	705
5	100600	600	65	108432	720
10	101205	605	70	109169	737
15	101814	609	75	109925	756
20	102430	616	80	110699	774
25	103053	623	85	111493	794
30	103685	632	90	112309	816
35	104326	641	95	113147	838
40	104978	652	100	114008	861
45	105641	663	105	114893	885
50	106317	676	110	115804	911
55	107007	690	108·53	1·15534	—

The rate of expansion of di-isobutyl, obtained by the electrolysis of potassium valerianate, has already been determined by Kopp, who has expressed his observations by the formula—

$$V = 1 + 0.0012125t + 0.0000002793t^2 + 0.00000016297t^3.$$

This gives numbers in close accordance with those furnished by the formula deduced from my observations.

Mr. W. Carleton-Williams has also published a number of determinations of the specific gravity of di-isobutyl at different temperatures (*Chem. Soc. J.*, 1879, 125), but the rate of expansion calculated from

his observations is considerably less than that found by Kopp and myself.

	25°.	50°.	75°.	100°.
Kopp	10306	10633	10995	11404
Thorpe.....	10305	10633	10993	11401
Williams	—	10593	—	11322

Aniline, C₆H₅.NH₂.

The sample of aniline which served for my observations boiled absolutely constantly at 181·5°. $n = 64^\circ$, $t = 65^\circ$. Bar. 733·2. Corrected and reduced b. p., 183·7°.

Its specific gravity was found to be 1·02763 at 11·63° compared with water at 4°; this at 0°, and compared with water at 4°, becomes 1·03790.

Other observers have found—

	B. P.	Sp. gr.
Hofmann.....	182°	1·020 at 16°
Kopp	184·8 at 737·2°	1·0251 „ 13·7°
„	—	1·0361 „ 0°
Städeler and Arndt	184·5°	1·018 „ 15·5°
Lucius.....	182—183°	1·024 „ 17·5°

The following observations of its rate of expansion were made in Dilatometer E. In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
6·96	2818·6	2818·8	52·56	2929·2	2929·4
14·71	2837·3	2837·1	69·54	2973·1	2972·8
31·65	2877·9	2877·9	81·70	3012·6	3012·5

In the oil-bath :—

T°	t' .	T Δ .	V.	E.	Observed.	Calculated.
109·93	38·5	110·01	3069·2	208·9	3082·7	3082·8
116·87	44·1	117·02	3088·1	227·8	3103·3	3103·1
134·30	45·4	134·77	3133·3	273·0	3156·2	3156·2
146·12	49·1	147·01	3165·8	305·5	3194·4	3194·2

These numbers may be represented by the expression :—

$$2802\cdot383 + 2\cdot353\,77t + 0\cdot000\,712\,265t^2 + 0\cdot000\,009\,695\,7t^3,$$

which on dividing through by the first term, and correcting for the expansion of the glass (·00002303), becomes—

$$V = 1 + 0.00086295t + 0.000000273509t^2 + 0.0000000034656t^3,$$

which affords the numbers in the following table, showing the relative volume of aniline at every 5° between 0° and its boiling point.

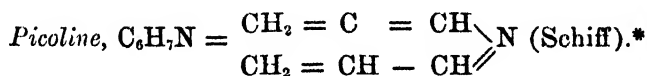
Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	100	109250	508
5	100432	432	105	109764	514
10	100866	434	110	110285	521
15	101302	436	115	110813	528
20	101740	438	120	111348	535
25	102180	440	125	111891	543
30	102623	443	130	112442	551
35	103069	446	135	113001	559
40	103518	449	140	113569	568
45	103970	452	145	114144	575
50	104426	456	150	114729	585
55	104887	461	155	115324	595
60	105351	464	160	115927	603
65	105820	469	165	116540	613
70	106294	474	170	117163	623
75	106772	478	175	117797	634
80	107256	484	180	118441	644
85	107746	490	185	119095	654
90	108241	495			
95	108742	501	183.7Δ	1.18924	—

The rate of expansion of aniline has already been determined by Kopp, who has expressed his results by the formula—

$$1 + 0.0008173t + 0.00000091910t^2 + 0.0000000062784t^3.$$

which gives slightly lower numbers than that afforded by the expression deduced from my observations:—

	0°.	50°.	100°.	150°.
Kopp	10000	10433	10915	11454
Thorpe	10000	10441	10925	11475



The picoline which served for my experiments was a portion of a large quantity prepared by the late Dr. Anderson. A platinum determination, made by Dr. Ramsay (to whom I am indebted for the sample), showed it to be pure.

* *Chem. Soc. J.*, 1871, 403.

After treatment with freshly burnt lime, it boiled between 133 and 134°, the greater portion coming over between 133·7 and 134°. Bar., 746·4 mm. $n = 0$. Corrected and reduced boiling point, 133·5°.

A determination of vapour-density yielded the following numbers:—

Weight of liquid	0·2018 gram
Volume of vapour	106·7 c.c.
Temperature	122·5°
Barometer	744·2 mm.
Height of column	240·3 „

Found 46·77 Calculated 46·50

A determination of specific gravity gave 0·95257 at 10·0°, compared with water at the same temperature. This at 0°, compared with water at 4°, becomes 0·96161.

Other observations on record are—

Anderson.....	133—135°	0·9613 at 0°
Thenius	134°	0·933 „ 22

The following observations were made with Dilatometer C. In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2982·7	2982·4	36·75	3089·8	3089·7
12·39	3017·6	3017·6	47·10	3121·8	3121·6
24·25	3052·1	3052·2	61·19	3166·4	3166·6

In the oil-bath:—

T° .	t .	$T\Delta$.	V.	E.	Observed.	Calculated.
62·49	18·8	62·38	3162·9	168·2	3170·5	3170·5
73·48	21·1	73·50	3196·6	207·9	3207·5	3207·5
89·12	25·2	89·35	3245·5	250·8	3262·6	3262·7
97·69	28·2	98·03	3273·4	278·7	3294·4	3294·2
116·00	28·8	116·18	3329·8	335·1	3362·3	3363·2
122·05	32·3	122·30	3351·7	357·0	3387·9	3387·5
130·64	35·7	131·06	3381·6	386·9	3423·9	3423·3

These observations may be represented by the expression—

$$2982·443 + 2·808\ 965t + 0·002\ 453\ 472t^2 + 0·000\ 013\ 560t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (·0000247), becomes—

$$V = 1 + 0·000\ 966\ 534t + 0·000\ 000\ 845\ 901t^2 + 0·000\ 000\ 004\ 566\ 9t^3.$$

By the aid of this formula the following table, showing the relative volume of picoline at every 5° between 0° and 135° , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	75	107917	580
5	100485	485	80	108507	590
10	100975	490	85	109107	600
15	101470	495	90	109717	610
20	101971	501	95	110337	620
25	102476	505	100	110968	631
30	102988	512	105	111610	642
35	103506	518	110	112263	653
40	104031	525	115	112928	665
45	104562	531	120	113606	678
50	105101	539	125	114296	690
55	105648	547	130	114998	702
60	106202	554	135	115714	716
65	106765	563			
70	107337	572	133.5	1154974	—

Nitrogen Tetroxide, N_2O_4 , or NO_2 .

A special interest attaches to the knowledge of the specific volume of nitrogen tetroxide by reason of the light which it is calculated to throw on the constitution of this substance. Moreover, as the group NO_2 plays an important part in many chemical compounds, such knowledge would presumably tend to elucidate the cause of the widely different volumes which nitrogen seems to possess in its various combinations.

A quantity of the liquid was therefore prepared by heating carefully dried lead nitrate in a hard glass retort, and a slow current of dry oxygen was passed through the strongly cooled product, to insure the oxidation of any trioxide which might be present. The tetroxide was then distilled in an apparatus composed wholly of glass. It boiled completely between 21.67° and 22.20° , the greater portion coming over between 21.7 and 21.95° ; $n = 22^{\circ}$, $t = 13.5^{\circ}$. Bar., 760.0 mm. Corrected and reduced boiling point, 21.64° .

Its specific gravity was found to be 1.4903 at 0° , compared with water at 4° . Dulong observed 1.461 (temperature not given), and the boiling point, 28° (*Schweig. J.*, 18, 177). The boiling point is given as 22° in *Watts's Dictionary*, 4, 76; the authority is not stated.

The following observations of the volume at different temperatures were made in Dilatometer D:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	3304·3	3304·6	12·42	3368·0	3368·2
4·18	3326·2	3326·2	13·83	3375·7	3375·5
5·89	3335·0	3334·9	16·00	3387·2	3387·1
8·01	3345·5	3345·6	17·58	3395·7	3395·7
9·94	3355·7	3355·4	19·46	3405·9	3405·6

These observations may be represented by the formula—

$$3304.594 + 5.187\ 52t - 0.013\ 228t^2 + 0.000\ 071\ 175t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (·0000213), becomes—

$$V = 1 + 0.001\ 591t - 0.000\ 003\ 970\ 15t^2 + 0.000\ 000\ 215\ 3t^3,$$

by means of which the following table, showing the relative volumes of nitrogen tetroxide at every 5° , between 0° and 25° , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	20	103196	826
5	100789	789	25	104065	869
10	101573	784			
15	102370	797	21·64	1·03523	—

The thermal expansion of this liquid has already been studied by Drion (*Ann. Chim. Phys.* [3], 56, 5), more particularly at temperatures above its ordinary boiling point, but our results cannot be strictly compared, as Drion's numbers are not corrected for the expansion of the glass.

In a subsequent communication I propose to give the results of my observations on the volatile chlorides of silicon, titanium, and tin, and of certain arsenic, phosphorus, vanadium, sulphur, and chromium derivatives; and finally to discuss the entire series and to indicate the bearing of the conclusions to which they lead on this question of the relation of the molecular weight of a body to its specific gravity as a liquid.

XVI.—CONTRIBUTIONS FROM THE LABORATORY OF THE UNIVERSITY OF TÔKIÔ, JAPAN.

II. *On Perthiocyanate of Silver.*

By R. W. ATKINSON, B.Sc. (Lond.), Professor of Analytical and Applied Chemistry in the University.

IN a communication presented to the Chemical Society (this Journal, 1877, 2, 254) I showed that the silver salt of perthiocyanic acid has the formula $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$, although, on account of the readiness with which it decomposes, the numbers obtained by analysis varied a little from the theoretical numbers. I also showed that the black precipitate obtained by boiling the yellow silver perthiocyanate with water varied in composition according to the treatment to which it had been subjected, the percentage of silver being greater when an excess of silver nitrate solution was used. The ratio of the numbers of atoms of silver and sulphur was found to vary, being in one case as 3 : 2, and in another as 17 : 10. I then conjectured that the variation was due to admixture of the silver sulphide, which forms the main product of the decomposition, with some substance containing a larger proportion of sulphur, and I was of opinion that this substance might be silver thiocyanate. Other matters have prevented me continuing the investigation until recently, but now I think I have obtained evidence in favour of a much simpler explanation, viz., that the substance containing a greater proportion of sulphur is undecomposed perthiocyanate, and that the extent of the decomposition is dependent upon the proportion of silver nitrate present, upon the temperature at which the decomposition is effected, and upon the time during which it is allowed to go on.

When the silver perthiocyanate was precipitated from an alcoholic solution of the acid and filtered off without boiling, the weight of the precipitate corresponded very nearly with that required by the formula $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$. The experimental numbers gave per molecule of acid ($\text{H}_2\text{C}_2\text{N}_2\text{S}_3 = 150$) 352, 370, 366.5, instead of 364 ($\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3 = 364$), and an amount of silver represented by the numbers 205, 220, 240, 219, 218, instead of 216 ($\text{Ag}_2 = 216$). When, however, the alcoholic solution was boiled, the weight of the precipitate formed when an excess of silver was used amounted in one case to 471, and in another to 521 per molecule of acid. The silver contained in the two precipitates weighed 434 and 432, almost exactly 4 mols. per molecule of acid.

When the silver perthiocyanate thrown down from an alcoholic solution of the acid was quickly filtered and washed, to remove the excess of silver nitrate, first with alcohol, then with water, and the precipitate afterwards boiled with water until no further change was apparent, the weight of the black precipitate was in three experiments 339, 342, and 300 per molecule of acid, and the weight of silver 261, 259, 232.

The supernatant liquid was coloured yellow, and the composition of the precipitate was probably that of a mixture of silver sulphide and perthiocyanate in nearly equal proportions, $\text{Ag}_2\text{S} + \text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$, which would require 306 of black precipitate, 216 of silver, and 62 of sulphur. The black precipitate contained in the three experiments above given 77.0, 75.8, and 77.7 per cent. of silver, the above formula requiring 70.6 per cent.

Having ascertained that in the decomposition of silver perthiocyanate 4 atoms of silver are necessary, and that, in order to gain the requisite amount, the silver salt itself splits up, a series of experiments under varying conditions was next instituted, first, to determine the weight and percentage of silver in the black precipitate when the proportion of silver nitrate added varied from 1 to 10 mols. per molecule of acid; secondly, to determine the influence which the duration of heating had upon the result, and, thirdly, to observe the effect of different temperatures upon the decomposition, it having been noticed on a previous occasion that the decomposition was much retarded at a temperature of $10-12^\circ$.

TABLE I.—*Experiments with varying proportions of Silver.*

	Number of atoms of silver added.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Percentage of silver in the black pre- cipitate.
a	1	127.5	108	84.7
b	2	261.2	216	82.7
c	3	386.0	324	83.9
d	4	513.9	432	84.1
e	5	622.2	540	86.8
f	6	659.0	574	87.1
g	10 ($\frac{1}{2}$ hour)	650.0	538	82.8
h	10 (1 hour)	644.0	526	81.6
k	10 ($1\frac{1}{2}$ hour)	612.0	490	80.2

The liquids of the first six experiments were boiled for about 20 minutes, and are quite comparable amongst themselves; but the solutions to which 10 atoms of silver had been added were boiled for the length of time mentioned in each case, and it will be noticed that

the weight of the black precipitate, the weight and the percentage of silver, all show a tendency to decrease on long boiling.

Considering the first six experiments, however, it will be observed that, up to the addition of 5 atoms of silver, the weight of silver contained in the precipitate increases proportionately, none whatever going into solution. With 6 atoms of silver added the whole of the silver was not thrown down, but sufficient to give a precipitate containing 87.1 per cent., and thus pure silver sulphide. With the exception of the first experiment the percentage of silver increases with the increased proportion of silver added, and this shows that the black precipitate contains more and more silver sulphide in proportion as the amount of silver added is greater. Assuming that the precipitate consists of a mixture of silver sulphide and perthiocyanate, we may calculate the proportion of each substance present in the above experiments:—

TABLE II.

	Percentage of Ag_2S .	Percentage of $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$.
<i>b</i>	84.9	15.1
<i>c</i>	88.5	11.5
<i>d</i>	89.2	10.8
<i>e</i>	98.9	1.1
<i>f</i>	100.0	0.0

This table shows very clearly the progress of the decomposition of the silver perthiocyanate under the influence of increasing quantities of silver nitrate. To test the action of nitric acid, two experiments were made—1st, one in which an amount of the acid equivalent to 2 mols. of HNO_3 was added, so that, on boiling, the liquid would contain 6 mols. of HNO_3 per molecule of perthiocyanic acid, and, 2nd, an experiment in which an amount of pure precipitated calcium carbonate was added in quantity just sufficient to neutralise the nitric acid that would be liberated in the course of the reaction. The liquids were then boiled for one hour, 4 atoms of silver being added.

TABLE III.

No.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Per- centage of silver.	Remarks.
1	457	365	80.0	Excess of nitric acid.
2	540	401	74.3	Calcium carbonate added.
3	518	428	82.6	No addition.

The effect of the increased quantity of nitric acid is thus to reduce the weight of the black precipitate, the weight of silver, and the percentage below those obtained without the addition of nitric acid. The addition of calcium carbonate, by neutralising the acid liberated, permits the formation of the two silver compounds in nearly equal proportions, the percentage 74·3 corresponding to 54 per cent. of silver sulphide, the weight of the black precipitate also being greater than when no calcium carbonate was present. It appears that the nitric acid acts first upon the silver perthiocyanate, and only when this is completely decomposed does it begin to touch the silver sulphide.

At temperatures below 100° C. the change on protracted boiling is not very marked, as will be seen from the following numbers. The temperature in each experiment was 50°, and the times one, two, and four hours respectively, the number of atoms of silver added being four.

TABLE IV.—*Four Atoms of Silver. Temperature 50°.*

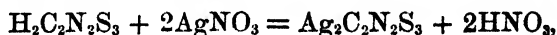
No. of hours.	Weight of the black precipitate per molecule of acid.	Weight of silver in the precipitate per molecule of acid.	Percentage of silver.	Percentage of Ag ₂ S in the black precipitate (calculated).
1	498·0	392	78·8	70·0
2	541·5	408	75·3	57·5
4	542·5	411	75·8	59·3

It will be observed that the results are practically the same whether the precipitate be heated to 50° for two hours or for four hours. The effect of temperature upon the reaction is shown in the following table, which gives the results of experiments at the temperatures mentioned, the amount of silver added being 4 atoms per molecule of perthiocyanic acid, and the time of heating one hour. The numbers at 50° are the same as those for one hour given in the preceding table:—

TABLE V.—*Four Atoms of Silver. Time, one Hour.*

Temperature.	Weight of the black precipitate per molecule of acid.	Weight of silver in the black precipitate per molecule of acid.	Percentage of silver.	Weight of free acid liberated per molecule of H ₂ C ₂ N ₂ S ₃ .
20° C. ..	361	222	61·5	140
50 " ..	498	392	78·8	253
100 " ..	518	428	82·6	230

From these experiments it is evident that at 20° the silver perthiocyanate was very slightly decomposed, the amount of silver sulphide, however, being sufficient to blacken it completely. This is confirmed by the amount of nitric acid contained in the filtrate, that corresponding to a decomposition—



being 126 per molecule of $\text{H}_2\text{C}_2\text{N}_2\text{S}_3$ against 140 found.

A little more than 2 mols. of silver nitrate was decomposed, resulting in the formation of some silver sulphide. At 50° in the same time the decomposition was much greater, the amount of nitric acid liberated corresponding almost exactly with 4 mols. At 100° the decomposition is still more pronounced, although boiling for one hour was not enough to make it complete. The percentage of silver sulphide at the three temperatures is given below.

TABLE VI.

Temperature.	Percentage of Ag_2S .	Percentage of $\text{Ag}_2\text{C}_2\text{N}_2\text{S}_3$.
20° C.	7·9	92·1
50 „	70·0	30·0
100 „	83·8	16·2

The changes at the three temperatures can be shown by a comparison of the amounts of silver and sulphur contained in the precipitate. The ratio of the number of atoms is as follows:—

TABLE VII.

Temperature	Ratio of the atoms of	
	Silver.	Sulphur.
20° C.	0·815	1·000
50 „	1·180	1·000
100 „	2·150	1·000

Thus at 20° the ratio approaches that in the silver perthiocyanate, *i.e.*, as 67 : 1, whilst the ratio increases at higher temperatures, until at 100° it is approximately 2 : 1, the ratio in which they exist in silver sulphide.

As further confirmation a specimen of the black precipitate which

had accumulated during these experiments was analysed, and found to contain—

Ag.....	82.15 per cent.
S	14.71 „
C	1.31 „
H	0.13 „
N (diff.)	1.70 „

100.00

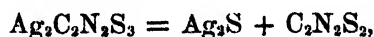
The percentage of silver, assuming the precipitate to contain only silver sulphide and perthiocyanate would be—

Ag ₂ S	82.2 per cent.
Ag ₂ C ₂ N ₂ S ₃	17.8 „
<hr/>	
100.0	

a mixture which would require the following percentages:—

Ag	82.16 per cent.
S	15.30 „
C	1.17 „
N	1.37 „
<hr/>	
100.00	

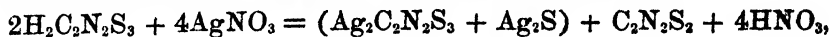
The agreement of the calculated percentage with that actually found is sufficiently close to prove that the precipitate does consist of the two substances mentioned above. As a final test of this being the true explanation of the reaction, 0.1304 gram of silver nitrate in alcoholic solution was added to an excess of perthiocyanic acid, also dissolved in alcohol, and kept during the experiment at as low a temperature as possible. The bright yellow silver perthiocyanate, under these circumstances, preserves its colour and appears to undergo no decomposition. The precipitate was then thrown on a filter, well washed with alcohol, and, when no more was dissolved, the alcohol was replaced by water, and the silver precipitate afterwards washed into a beaker, and boiled with water for about half an hour. The whole was then filtered, and the precipitate, after drying, weighed 0.0974 gram, and, as it contained the whole of the silver added, there was thus 85.04 per cent. of silver. This corresponds with 92.6 per cent. of silver sulphide and 7.4 per cent. of silver perthiocyanate. If the silver sulphide, amounting to $\frac{92.6}{100} \times 0.0974 = 0.0902$ gram, had been formed according to the equation—



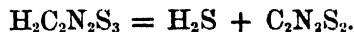
the corresponding amount of silver perthiocyanate decomposed would

be $\frac{364}{248} \times 0.0902 = 0.1324$ gram, and this, added to the amount of the undecomposed silver persulphocyanate, $= \frac{7.4}{100} \times 0.0974 = 0.0072$ would be $0.1324 + 0.0072 = 0.1396$, a sufficiently near approximation to the number 0.140, the amount of silver perthiocyanate actually used calculated from the weight of silver nitrate.

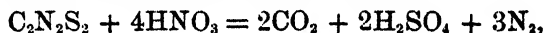
The nature of the decomposition of the silver perthiocyanate is, therefore, sufficiently clear, and may be formulated thus:—



and the actual proportions of the two insoluble silver salts will depend upon the conditions of the experiment as to time, temperature, and proportion of free acid present. The only point not yet cleared up is the existence of the compound $\text{C}_2\text{N}_2\text{S}_2$, cyanogen disulphide:—



The corresponding cyanogen monosulphide, $(\text{CN})_2\text{S}$, formed from thiocyanic acid, is known, but I have hitherto been unable to isolate the higher sulpho-compound. It is possible that during the heating with nitric acid, it may be decomposed thus:—



which is rendered probable by the fact that during the experiment some gas is evolved. I am at present examining the orange-red sublimate which forms when the dry silver perthiocyanate is heated, in the hope that it may contain the missing body.

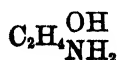
In conclusion, I wish to thank my assistant, Mr. Nakazawa, for his assistance in carrying out some of these experiments.

XVII.—On Methylated Dioxethylenamines.

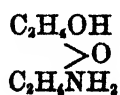
By H. F. MORLEY, M.A.

It is well known that the discovery of the oxethylene bases is due to Wurtz (*Ann. Chem. Pharm.*, **114**, 51; **121**, 226), who some twenty years ago showed that oxide of ethylene unites directly with ammonia to form the following bodies:—

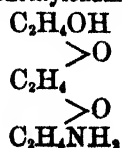
Oxethylenamine.



Dioxethylenamine.

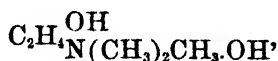


Trioxethylenamine.



He also showed that glycolic chlorhydrin is converted by ammonia into the first two bases, and that when heated with trioxethylenamine it yields tetra-, pent-, and even hept-oxethylenamine.

It was even then suggested by Strecker (*Compt. rend.*, **52**, 1279) that his choline might be related to these bases; but it was not until five years later that Liebreich's neurine, which Dybkowsky (*J. pr. Chem.*, **100**, 191) showed to be identical with choline, was converted by Baeyer (*Ann. Chem. Pharm.*, **140**, 306; **142**, 322) into the iodide $N(CH_3)_3(C_2H_4I)$, and thus proved to be trimethyloxethylenammonium hydrate:—



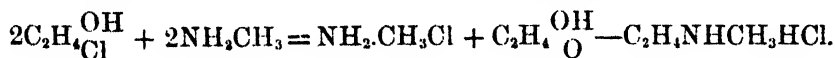
a view which was shortly afterwards confirmed by Wurtz (*Ann. Chem. Pharm.*, Suppl., **6**, 116, 197), who produced neurine chloride synthetically by heating glycollic chlorhydrin or ethylenic oxide with a solution of trimethylamine. The corresponding ethyl-compound derived from triethylamine and ethylene oxide, and oxamylenamine, a base isomeric with neurine (Wurtz: *Ann. Chem. Pharm.*, **7**, 88), complete the list, as far as the fatty series is concerned, of known members of the group under discussion,* but no one has sought for the intermediate members:—



Accordingly, at the instance of Professor Hofmann, I have examined the action of mono- and di-methylamine on glycollic chlorhydrin, and have found that in both cases a condensation takes place, almost the only product of the reaction being a homologue of $C_2H_4(OH)OC_2H_4NH_2$.

Monomethyldioxethylenamine.

17 grams of glycollic chlorhydrin (prepared by Carius's method from chloride of sulphur and glycol, which yields rather more than 50 per cent.) were heated to 100° for several hours with an excess of methylamine in aqueous solution. The reaction is as follows:



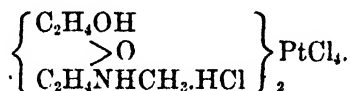
In order to get rid of the methylamine hydrochloride, the contents of the tubes were treated with oxide of silver and freed from methylamine by boiling. The solution, after being acidified and filtered, yields on evaporation over the water-bath a non-crystallisable syrup; to remove the last traces of silver chloride it is necessary to redissolve this in water, which produces a slight precipitate. The syrup ob-

* Demole has obtained oxethylenanilin, oxethylenetoluidin, &c. (*Ber.*, 1873, 1024; 1874, 635.)

tained by evaporating the filtrate was dissolved in absolute alcohol and precipitated with a concentrated solution of platonic chloride; and the semi-fluid precipitate was dissolved in water, and partly thrown down as an oil by adding alcohol. On further adding alcohol by small portions at a time, and at the same time stirring the liquid, a mass of small crystals was obtained. These were dissolved in water, and alcohol was added till the liquid became turbid. On standing, the liquid deposited a mass of splendid orange-red prisms, which gave by analysis the following results:—

	Calculated for $C_{10}H_{28}N_2O_4PtCl_6$.	Found.
C	18.46	18.82
H	4.31	4.65
N	4.31	4.34
Pt	30.31	30.15

The crystals therefore consist of the platinum salt of methyl-dioxethylenamine.



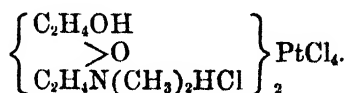
The oily precipitate gradually became solid, but nevertheless melted below 100° (which the crystals do not do); it contains 29.89 per cent. platinum, so that it consists principally of the same compound as the crystals.

Dimethyldioxethylenamine.

The product of the action of glycollic chlorhydrin (20 grams) on a solution of dimethylamine at 100° was treated in like manner with silver oxide. The hydrochloride of the new base is also a thick syrup; out of its alcoholic solution chloride of platinum precipitates a solid salt, which may be obtained by crystallisation from hot dilute alcohol in the form of small yellow crystals, whose analysis gave:—

	Calculated for $C_{12}H_{32}N_2O_4PtCl_6$.	Found.
C	21.24	20.99
H	4.72	4.95
N	4.13	4.42
Pt	29.06	28.71

agreeing with the formula for the platinum salt of dimethyl-dioxethylenamine:—



It is, therefore, homologous to the body previously described.

XVIII.—*Note on Igasurine.*

By W. A. SHENSTONE.

THE three alkaloids said to be present in the seeds of *Strychnos nuxvomica* all have poisonous properties ascribed to them, and it is noteworthy that these differ only in degree, strychnine being by far the most active, brucine the least. In some experiments described in a paper read before the Pharmaceutical Society in December, 1877 (*Pharm. Journ.*, Dec. 8, 1877), I showed that commercial brucine contains quantities of strychnine varying from 1 to $\frac{1}{4}$ per cent., and I suggested that its physiological action might be due to this circumstance; and this seems the more probable as Dragendorf, and, independently, I myself have obtained small quantities of strychnine from false Angostura bark, from which Pelletier and Caventou originally obtained the brucine with which they experimented, and which they believed to be free from the former alkaloid.

Igasurine is said by its discoverer Desnoix (*J. Pharm.* [3], 25. 202) to differ from brucine in its solubility in water, and in its activity as a poison; on the other hand, Jørgensen (*J. pr. Chem.* [2], iii, 175) has found a specimen of reputed igasurine to consist of brucine only. These various statements, and the observations cited above, have made me find it interesting to prepare some alkaloid from the source from which Desnoix obtained his so-called igasurine, and to examine it, particularly with regard to the presence of strychnine. Four gallons of an aqueous decoction of nuxvomica beans, from which the alkaloids had been precipitated by boiling with lime, were obtained (through the kind interest of Messrs. Hopkins and Williams), and after neutralisation, were evaporated on the water-bath to half a litre, or rather less; the product, which was astonishingly free from gummy matters, was rendered alkaline with ammonia, and a precipitate which fell separated. The mother-liquor, which still contained much alkaloid, was precipitated with tannin, and the alkaloid obtained from the precipitate by pressing it, mixing with excess of calcium hydrate, drying, and exhausting with boiling rectified spirit, by which means the whole of the residual alkaloids were obtained. The two products were separately treated with dilute alcohol. In each case the greater part dissolved, while a smaller portion remained insoluble, and, after recrystallisation, gave the reaction of strychnine. The soluble portions on examination were found to have the ordinary characters of brucine. I did not examine these minutely, as I have found that the brucine of commerce does not always present identical characters, and I suspect

it to be a mixture of an alkaloïd present in the *nux vomica* beans, and another body, probably a saponification product, in variable proportions. I have a considerable supply of brucine in my possession, which I have prepared by a special process, and I am now engaged in examining it, with a view to deciding this and other points.

The amount of strychnine obtained was in the part precipitated by ammonia at least 5 per cent. ; in the other portion somewhat less, and there can be no doubt that a further portion in each case went into solution with the brucine.

These results I think sufficiently explain the superior activity of Desnoix's alkaloïd to that of brucine, and go, with Jörgensen's observations, to show that the igasurine of Desnoix was not brucine, but a mixture of that substance with strychnine,—its other character, *i.e.*, its superior solubility, being of little weight, as the solubility of brucine and of some of its salts varies considerably with their degree of purity.

XIX.—*On some Reactions of Tertiary Butyl Iodide.*

By LEONARD DOBBIN. (Frankland Prize of the Institute of Chemistry.)

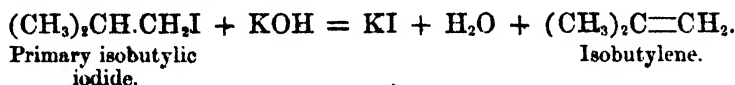
THE research, the report of which is contained in the following pages, was carried out in the University Laboratory, Würzburg, under the direction of Professor Wislicenus, and it comprises the investigation of three reactions of tertiary butyl iodide.

Preparation of the Tertiary Butyl Iodide.

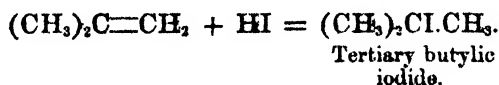
The starting material is primary isobutyl alcohol, which is converted into the corresponding primary iodide by the usual method for preparation of iodides of the alcohol radicals by means of amorphous phosphorus and iodine. On rectification the portion of the distillate collected for several degrees below and above the boiling point of the pure primary iodide (120.5°) was employed for the further reactions to obtain the tertiary iodide. The first of these consisted in the preparation of isobutylene, which was effected by decomposing the iodide with potassium hydrate.

A large flask containing a concentrated alcoholic solution of potassium hydrate, into which the iodide could be allowed to flow from a dropping-funnel, was connected with an inverted condenser, and from the end of the condenser a tube led to a gas-holder. The potassium hydrate solution was first heated on a water-bath until the alcohol

began to boil, when the iodide was allowed to flow in drop by drop and, as the latter was decomposed, the isobutylene formed passed into the gas-holder. In this way isobutylene could be rapidly prepared, but the product always fell considerably short of the calculated quantity. Some isobutylene was also prepared by heating slightly diluted sulphuric acid with isobutyl alcohol in presence of sand or powdered talc, but the quantity of gas obtained in this way was only a small proportion of the calculated quantity, as large quantities of polymerised hydrocarbons were always formed. The method was given up, as it was not so satisfactory as that with the iodide. The collected isobutylene was then passed into a saturated, strongly fuming solution of hydriodic acid. The latter solution was placed in a bottle which was provided with an india-rubber stopper, through which passed a single tube reaching down to the liquid. The air was first driven out of the bottle by allowing a rapid stream of isobutylene to pass through for a few seconds, the stopper was then firmly placed in the bottle, when absorption, assisted by vigorous shaking and cooling with ice, took place very rapidly, tertiary isobutyl iodide being formed. Equations will render the reactions clear:—



then:—



The product thus obtained was separated from the aqueous hydriodic acid solution, treated with dilute potassium hydrate solution to remove hydriodic acid and free iodine, carefully dried with calcium, and filtered. It was then in the condition in which it was used for the subsequent experiments.

I. DECOMPOSITION WITH WATER.

In the course of some experiments made in the endeavour to discover a good method for the preparation of tertiary butyl cyanide, $(\text{CH}_3)_3\text{C}(\text{CN}).\text{CH}_3$, a quantity of tertiary butyl iodide was shaken up with excess of a 12 per cent. solution of hydrocyanic acid. It was found that on prolonged shaking the iodide was gradually dissolved in the other liquid, until at length a quite homogeneous liquid was obtained. Excess of zinc oxide was then added to combine with the hydriodic acid and excess of hydrocyanic acid present. Zinc iodide and cyanide were formed and the liquid was then subjected to distillation. It began to boil at 63° , between which point and 100° a con-

siderable portion of it passed over. At 100° scarcely anything but water distilled. The distillate, which was a slightly yellow, thickish liquid, was clearly a very different body from the cyanide sought for, as it was readily soluble in water, which the cyanide is not, and the latter only begins to boil at about 105° . On placing it in a mixture of snow and salt it solidified at about -7° in star-like crystalline masses, and its properties in general led to the idea that it might be the alcohol corresponding to the tertiary iodide, trimethylcarbinol, or rather the molecular compound which this body forms with water, $2[(\text{CH}_3)_3\text{C}(\text{OH})\cdot\text{CH}_3] + \text{H}_2\text{O}$.

Acting on this idea, the liquid was dried partially by adding dried potassium carbonate, and then it was completely freed from water by repeated distillation with barium oxide. After this treatment the body exhibited all the properties of trimethylcarbinol. It solidified in characteristic semi-transparent crystalline masses, which melted at 25.5° and the liquid boiled at $82-82.5^{\circ}$.

Combustions gave the following numbers:—

I. .0857 gram substance gave .1074 gram OH_2 and .2026 gram CO_2 .

II. .1302 gram substance gave .1596 gram OH_2 and .3097 gram CO_2 .

		Found.	
		I.	II.
C	Calculated for $\text{C}_4\text{H}_9\text{OH}$ 64.86 per cent.	64.47	64.87
H 13.51 „	13.92	13.62
O 21.63 „	—	—

As it was believed that in this reaction the hydrocyanic acid did not play any part, a second experiment was made in order to ascertain whether such was really the case. 20 grams tertiary isobutyl iodide were vigorously shaken with 50 grams distilled water. On leaving the liquid for two days, with occasional shaking, it was found that the iodide had all dissolved in the water, and that the liquid, which at first had been very slightly acid, now gave a very marked acid reaction with blue litmus paper. Excess of sodium carbonate was then added, when carbon dioxide was evolved in considerable quantity; potassium hydrate solution was added till the coloration due to iodine had disappeared; then, after nearly neutralising with hydrochloric acid, the liquid was distilled. It began to boil at 63° , the temperature rose rapidly to 84° , where it was constant for some time, and then rose gradually to 100° . The distillate below 100° was, as before, partially dried with potassium carbonate, and then completely dried by repeated distillation from barium oxide. Determination of melting point gave $25-25.5^{\circ}$, that of boiling point 82.5° .

Combustions gave the following numbers:—

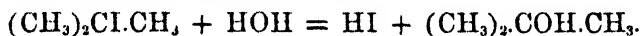
I. .0925 gram substance gave .1164 gram OH_2 and .2202 gram CO_2 .

II. .0935 gram substance gave .1174 gram OH_2 and .2219 gram CO_2 .

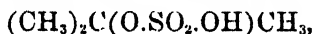
	Calculated for $\text{C}_4\text{H}_9\text{OH}$.	Found.	
C	64.86 per cent.	64.92	64.72
H	13.51 „	13.98	13.95
O	21.63 „	—	—

The total quantity of pure substance obtained from this reaction was 4.2 grams, the calculated quantity being 7.9 grams, therefore the process would seem to give very good results, as there was, of course, considerable loss in repeatedly distilling the small quantity from barium oxide.

The reaction may be expressed thus:—



This action of water is analogous to its reaction upon the compound formed by absorbing isobutylene in sulphuric acid—



which also gives trimethyl-carbinol, but it is the first example of an iodide of an alcohol radical being decomposed by water at ordinary temperatures. The temperature at which the action took place was, in the first case, below 0° , and in the second below 10° .

II. DECOMPOSITION WITH ZINC OXIDE.

During some of the experiments made in the foregoing it was found that zinc oxide acted upon tertiary isobutyl iodide in absence of water, especially on gently heating the iodide and adding dry zinc oxide in small quantities. If much zinc oxide were added at once, the reaction became rather violent, isobutylene was formed in considerable quantity, and a large amount of heat was evolved.

26 grams of carefully dried iodide were mixed gradually with the calculated quantity of dry zinc oxide to combine with all the iodine present, the temperature being kept at about 15° by cooling with water. A slight excess of zinc oxide failed to produce any further reaction. The liquid, which was previously dark brown from the presence of free iodine, was now nearly colourless, and the peculiar odour of the iodide was replaced by a pleasant ethereal odour.

It was distilled directly from the precipitated zinc iodide on an oil-bath. The distillate consisted of two layers, the under one of which

was only a very small quantity and was found to be water formed in the reaction. After separating the latter by means of a small separating funnel the upper liquid, which weighed 3.5 grams, was dried with calcium chloride and distilled. It began to boil at about 90° , but the temperature rose rapidly to 170° , only 1.3 grams coming over between 140° and that point. The remainder, weighing 2 grams, distilled between 170° and 180° , the boiling point remaining constant for some time at 175° . The fractions, $160-170^{\circ}$ and $170-180^{\circ}$, were again distilled, and here the principal fraction, weighing 0.9 gram, distilled between 174° and 176° . This fraction was used for the analyses and for the vapour-density determination.

Combustions gave the following numbers:—

I. .1949 gram substance gave .2503 gram OH_2 and .6121 gram CO_2 .

II. .1569 gram substance gave .2043 gram OH_2 and .4927 gram CO_2 .

Calculated for $(\text{CH}_2)_n$.		Found.	
C	85.71	85.65	85.64
H	14.28	14.26	14.46
	<hr/> 99.99	<hr/> 99.91	<hr/> 100.10

Vapour-density Determination (Hofmann's Method).

Weight of substance taken	0.1762 gram	= P
Observed column of vapour	106.4 c.c.	= V
Height of mercury column above level		
in trough	463.6 mm.	= H
Height of barometer	749.3 "	= B
Boiling point of aniline	182° C.	= t
Temperature of room	15° C.	= t'
Tension of mercury vapour at 182° C. .	11.89 mm.	= T
Mercury column corrected to t'		= H'
Vapour-density required		= D

$$H' = H[1 - .00018(t - t')].$$

$$H' = 463.6[1 - .00018(182 - 15)].$$

$$H' = 449.7 \text{ mm.}$$

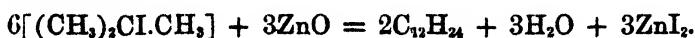
$$D = \frac{P \cdot (1 + .00367t) \cdot 760}{.0012932 \cdot V(B - H' - T)} \quad (\text{air} = 1).$$

$$D = \frac{.1762 \cdot (1 + .00367 \cdot 182^{\circ}) \cdot 760}{.0012932 \cdot 106.4(749.3 - 449.7 - 11.89)}$$

$$D = 5.642.$$

$$D \text{ calculated for } (\text{C}_2\text{H}_6)_2 = 5.805.$$

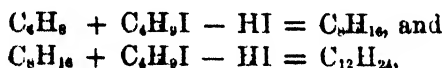
From these determinations there could be no doubt that the body was isobutylene, the formation of which may be expressed by the following equation:—



It may be well to mention a paper by Lermontoff approaching this subject, which has recently been published (*Annalen*, 196, 116).

Lermontoff saturated tertiary isobutyl iodide with isobutylene at -10° , 15 grams absorbing 7 to 8 litres of the gas. The solution thus obtained was sealed in a tube with twice its weight of calcium oxide, and the whole was heated for 20 hours to 100° . Excess of isobutylene must be present in order that the product may not be considerably reduced in quantity. After the end of the reaction the liquid product on distilling off and fractionating proved to consist of two bodies: isodibutylene, b. p. 102.5° , and isobutylene, b. p. 177.5° to 178.5° . Zinc oxide or magnesium oxide gave the same result.

In this reaction the isobutylene formed by the action of calcium oxide upon tertiary isobutyl iodide is supposed to unite with the isobutylene already present, forming the polymerides, and the following equations are given:—



but, as quantitative results are not given, it cannot be ascertained whether a greater quantity of the mixed polymerides was formed than could have been formed from the iodide alone.

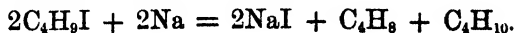
In the present experiments, now published for the first time, the action took place at ordinary temperatures, and isobutylene was not formed, or if at all, only in very small quantity, the weight of the distillate obtained on fractionating, between 20° and 140° , being only 0.1 gram, or about $\frac{1}{80}$ th of the whole.

Lermontoff does not mention in her paper whether the isobutylene had all been changed into polymerides by the heating in closed tubes, which is certainly a very important point in the reaction.

III. DECOMPOSITION BY SODIUM.

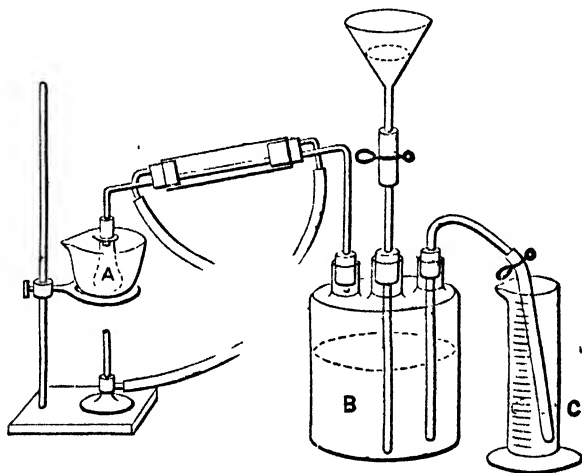
Professor Wislicenus observed that when tertiary butyl iodide was acted upon by sodium a gas was formed, a considerable quantity of which was absorbed by passing it through bromine, but the unabsorbed gas still burned with a luminous flame. At his suggestion this investigation was taken up, in order to ascertain whether or not the resultant gas consisted of isobutylene and isobutane, and if it did,

whether they were formed in equal volumes, as would be the case if the reaction were simply the following:—



The volume of the gas formed was first approximately measured by using an apparatus for the decomposition, which the accompanying sketch represents.

10 grams tertiary butyl iodide were placed with a weighed quantity of sodium (the former being in excess) in the flask A, which was then heated for several hours in a water-bath. The gas formed, mixed with the air originally in the flask and condenser tube, passed over into the Woulfe's bottle B, whilst water was driven from the latter into the graduated cylinder C. When the level in C ceased to rise the whole was allowed to become quite cold, the levels in B and C



were made to correspond, and then the volume of water in C was noted, as well as the temperature, and the pressure of the atmosphere.

In two experiments the results agreed almost exactly with each other. The corrected volumes of gas obtained in the two cases calculated out and compared with 1 gram sodium were 630·8 c.c. and 630·5 c.c. respectively. These very close results must, however, be taken with care, as in neither case had all the sodium been used up, it having become surrounded by a covering of sodium iodide which prevented further action. The quantities left unchanged were, however, very small.

The gas thus obtained was collected in a series of tubes and was subsequently analysed. The air with which it was mixed was not estimated, as only the relative proportions of the gases formed by the

reaction were wanted, and, previous to analyses, the gas was accidentally mixed with more air than it had at first contained.

The analyses were made with Bunsen's apparatus, and the absorption tube and eudiometer were specially calibrated for these analyses. Previous to any of the experiments the whole quantity of the gas used was dried with a bullet of potassic hydrate.

The following are the various analyses made:—

I. Absorption of the Olefine.

This was accomplished in the absorption tube by means of coke bullets saturated with fuming sulphuric acid, a fresh bullet being introduced every two hours, until the last one, on removal after this time, still fumed strongly. A potash bullet was then introduced to remove acid fumes and free sulphuric acid.

II. Combustion of the Residual Gas after Absorption of the Olefine.

The gas was brought into the eudiometer, at the top of which a drop of water had been placed to saturate the gas with moisture; oxygen was then added, and the mixture was exploded by a spark from an induction coil. The contraction was measured, then a potash bullet was introduced to absorb the carbon dioxide formed.

III. Estimation of the Value of n in the Olefine.

This was done with a portion of the original gas which had not been treated with fuming sulphuric acid, and the method was similar to that employed in II.

The numbers obtained from the observations were as follow:—

	Observed volume. mm.	Corrected vol. from calibration table, including correction for meniscus.	Level of mercury in trough. mm.	Temperature. °C.	Barometer. mm.	Corrected volume at 0° C. and 1,000 mm.
<i>I. Absorption of Olefine.</i>						
* Gas taken	103·5	102·46	236·8	5·0	747·4	61·79
* After bullets of fuming sulphuric acid and KOH.....	89·3 91·0	88·00 89·73	236·0 237·8	1·6 2·0	737·4 726·0	51·68 51·48
<i>II. Combustion of the Residual Gas.</i>						
1.						
Gas taken.....	125·3	131·18	786·0	-2·4	759·6	12·59
+ Oxygen	216·7	224·02	785·2	-2·0	759·6	42·23
After explosion.....	206·2	213·41	785·7	-1·1	759·2	37·60
*After absorption of CO ₂	203·9	211·09	786·5	+1·0	758·0	36·89
2.						
Gas taken.....	129·0	134·94	787·4	-2·7	762·0	13·30
+ Oxygen	215·1	222·40	788·5	-2·6	762·0	41·53
After explosion.....	203·1	210·29	786·8	-2·2	760·1	36·57
*After absorption of CO ₂	197·5	204·63	787·1	-5·6	761·5	35·83
<i>III. Value of n in Olefine.</i>						
Gas taken.....	144·0	150·23	784·9	5·4	747·0	14·64
+ Oxygen	356·7	365·40	784·0	4·0	744·1	111·90
After explosion	340·3	349·00	784·5	4·5	742·7	100·33
*After absorption of CO ₂	328·9	337·56	796·3	1·8	737·1	90·45

Calculation of Results.

In I the percentage was calculated directly.

In II the carbonic dioxide formed was taken as representing isobutane, C₄H₁₀. This, however, was only a very small quantity, whilst the contraction on explosion was considerable, showing that hydrogen must be present in large quantity.

$$x = \text{C}_4\text{H}_{10}, y = \text{H}_2, C = \text{contraction}, D = \text{CO}_2 \text{ formed.}$$

By the equation:—

2C₄H₁₀ + 13O₂ = 8CO₂ + 10H₂O, 1 volume C₄H₁₀, requires for combustion 6·5 volumes oxygen, forming 4 volumes CO₂, and the contraction is 3·5 volumes, therefore $x = \frac{D}{4}$.

* The observations marked thus denote that the gas was dry. In all others it was saturated with moisture.

The contraction due to C_4H_{10} is thus $\frac{3.5D}{4}$. Two-thirds of the re-

maining contraction is due to hydrogen, therefore $y = \frac{2\left(C - \frac{3.5D}{4}\right)}{3}$.

In III the amount of carbon dioxide which would have been formed by the mean of the quantities of isobutane found in II was subtracted from the whole quantity found, and the remainder was calculated as representing isobutylene, $x = C_4H_{10}$, $y = H_2$, $z = C_4H_8$.

C = contraction. $D = CO_2$ formed. $D' = CO_2$ formed by the quantity of isobutane present.

x being taken = mean of experiments in II, then $4x = D'$.

By the equation :—

$C_4H_8 + 6O_2 = 4CO_2 + 4H_2O$, 1 volume C_4H_8 requires for combustion 6 volumes oxygen, forming 4 volumes CO_2 , and the contraction

is 3 volumes, therefore $z = \frac{D - D'}{4}$ and $y = \frac{2\left(C - \frac{3D - D'}{4} - \frac{3.5D'}{4}\right)}{3}$
 $= \frac{2}{3}\left(C - \frac{3D + 2.5D'}{4}\right)$.

Calculated out, according to these formulæ, the results obtained were :—

	I.	II.		III.	
		1.	2.		
C_4H_8	16.52	—	—	15.74	} Percentages in original gas.
C_4H_{10}	—	1.12	1.16	(1.14)	
H_2	—	17.71	18.07	18.57	

These results were unexpected, as hydrogen had not been thought likely to be present.

In order that hydrogen should be formed it was necessary that the reaction should take place in this way :—



but in this case hydrogen would be formed in the proportion of one volume to two of isobutylene, whereas more than an equal volume was found. This was only explicable if part of the isobutylene had become polymerised, and to ascertain if such were the case the residual liquids from the action of sodium were examined. On mixing with water three layers were formed, the lowest of which was undecom-

posed iodide, and the middle one solution of sodic iodide in water. The upper liquid, which burned with a brightly illuminating flame, was separated by a pipette, dried with calcium chloride and then with sodium, and was then distilled. It began to boil at 152° , and all distilled below 182° , the principal quantity going over between 170° and 180° . The latter was distilled fractionally several times with metallic silver to remove free iodine. The endeavour to remove all the free iodine was not successful, as the whole quantity of liquid at this point weighed but 0.5 gram. A small portion was obtained boiling between 174° and 178° which had the ethereal oil odour of isotributylene, and although an analysis did not give good results, owing to the presence of iodine, there could be no doubt that this was the body which was formed.

Thus it would appear that by decomposing tertiary butyl iodide by means of sodium the bodies formed are isobutylene, isotributylene, and hydrogen, with small quantities of a hydrocarbon not absorbed by fuming sulphuric acid. It will be noted that here, as in the decomposition with zinc oxide, not a trace of isodibutylene was observed.

One more point was calculated out, viz.: whether the quantity of hydrogen found was such as should be formed if the reaction took place according to the last equation, but taking into account the formation of polymerised isobutylene and of isobutane, it was found that the quantity obtained was only about 75 per cent. of the theoretical quantity, supposing the sodium to have been completely combined with iodine. As, however, the sodium had not been entirely used up, the difference might be accounted for from that fact.

In conclusion, I wish to express my sincere thanks to Professor Wislicenus for masterly assistance rendered during the progress of the work.

ANNIVERSARY MEETING.

March 30th, 1880.

Dr. Warren De La Rue, F.R.S., President, in the Chair.

The following Report was read by the President:—

It is just eleven years ago that my second year of office as President came to an end, and it may be useful to compare the position of the Society at that period with its position now. In 1869, the number of Fellows was 522; there are now 1,034, or nearly double. Our total receipts in 1869 amounted to £1,122 19s. 8d. Our Treasurer's report shows that this year they are £2,720 6s. 6d., or more than double. During the year ending March 31st, 1869, 31 papers were read and three lectures were delivered at the Society's meetings, while in the past year we have had 75 papers and one lecture.

The Journal continues to increase in value and importance, as will be very evident if we refer back to 1869, when a modest volume of 457 pages comprised all that we published. The number of original papers in 1879 was 84, being an increase of 23 on the preceding year. These, together with the valuable Abstracts made by a most efficient staff of Abstractors, render our Journal the most complete compendium extant of the progress of Chemistry.

A glance through the pages of the last volume of our Journal cannot fail to render evident that many of the communications made at our Meetings are solid contributions to chemical knowledge, and that our Society has done its fair share of work. It must, therefore, be conceded that we have every reason for congratulation as regards the prosperity of the Society, the activity of its Members, and the value of its Journal.

Again, as regards the Library. During the past year a large number of books, costing nearly £500, has been added to it, and the Council are at present making arrangements for the preparation of a Card-catalogue, which, it is hoped, will give greatly increased facility of finding the books.

Although since my last term of office I have not been precisely in a sleepy hollow, like that described by Washington Irving, nevertheless my thoughts have been mainly absorbed by other branches of science, and I found myself, on returning to this chair, very much in the same

perplexity as *Rip Van Winkle* when he awoke in the *Kaatskill Mountains* after his long sleep.

So rapid has been the progress of our science, that much of the aspect of chemical thought has altered in the interval; old and once familiar bodies have not only changed their nomenclature, but new and unfamiliar individuals and families have crowded into the greatly extended domain of chemistry. The very elements which were looked upon as most stable are now considered to be in a critical position, and liable at any moment to dissociation: for it is only a few months ago that the minds of chemists were disturbed by the announcement that spectroscopic evidence afforded by the sun and stars tended to show that the so-called elements were in reality compound bodies. Even if we reserve our judgment on this point, we can no longer assert that the light emitted from the so-called elements, when incandescent or vaporised, is characterised by certain definite wave-lengths. Moreover, we learn that a well-known German chemist, Professor V. Meyer, has actually succeeded in dissociating the halogens chlorine, bromine, and iodine. The results which he and his coadjutors have obtained appear to leave little doubt that such is actually the case, and we must await the outcome of their continued labours with intense interest.

As regards the spectrum itself, we can no longer attribute certain specific functions and properties to different parts of it; for Captain Abney has shown that every part of the spectrum acts actinically, and he even goes so far as to hold out a prospect of Becquerel's beautiful discovery being further extended, so as to produce *permanent* photographs of the spectrum in its natural colours. In his Bakerian lecture to the Royal Society, Captain Abney has made known his method of preparing a form of silver bromide, sensitive not only to the ultra-violet and the whole visible spectrum, but also to the infra-red rays, and has presented to that Society his magnificent map of the infra-red spectrum. It is difficult to overrate the value of this discovery, and it may be expected that important results will accrue from the investigation of the infra-red absorption spectra of various substances. Indeed, Captain Abney has already informed me of his progress in this direction. The importance of photography, not only as affording a means of investigation, but as a method of permanently recording observations which may be dealt with at leisure, thus affording the means of accurate measurement, in such hands as those of Dewar, Liveing, and Abney, cannot be too highly prized.

A problem which had long baffled all efforts, the artificial production of the diamond, is said to have been solved. Mr. Hannay's communication on the subject is so vague, however, that it is impossible to pronounce any opinion on it. The observations on the solubility of solids in gases, which led Mr. Hannay to attempt to crystallise carbon,

and which are described in a recent communication to the Royal Society by Messrs. Hannay and Hogarth, are of great interest, and most important results will doubtless be obtained by an extension of these experiments.

The necessity for further information on the subject of the behaviour of various substances, and especially of mixtures under great pressure, is well shown by the recent remarkable observations of Cailletet, that on compressing a mixture of five volumes of carbon dioxide and one volume of air, the former at first liquefies; but that as the pressure is increased to 150—200 atmospheres, the meniscus of the liquid carbon dioxide becomes plane, and is gradually effaced until finally the liquid wholly disappears, apparently dissolving in the gas.

Mr. Ansdell's papers on the "Physical Constants of Liquid Acetylene and Liquid Hydrogen Chloride," as determined with the aid of the Cailletet apparatus in the laboratory of the Royal Institution, are valuable contributions to our knowledge of chemical physics, and appear to furnish the interesting result, that the volume of the liquid and gas are equal at the critical point in the case of the latter substance.

Another investigation in chemical physics of great interest is that recently published by Brühl, who has considerably extended the observations of Gladstone, Landolt, and others, on the refractive indices of carbon-compounds. The introduction of a new method of calculating the results, by which the influence of dispersion is eliminated, has led him to the discovery of an apparently very simple relation between chemical constitution and refractive power.

The extraordinary diligence of chemists who apply themselves to the investigation of carbon-compounds has also reaped a rich harvest of results. It would be impossible for me to consider the progress of this branch of chemistry in detail, but I cannot help noticing how rapidly the more complex bodies, such as the alkaloids and the carbohydrates, are being forced to yield up the secret of their constitution which has so long been withheld. The synthesis of Isatin by Claisen and Shadwell, and the researches of Baeyer in the Indigo-group, must, it would seem, ere long result in the discovery of a method for the artificial manufacture of this colouring matter.

Ladenburg's success in preparing the alkaloid atropine from Tropine and Tropic acid, the two substances which it furnishes when decomposed by hydration, is no doubt the first step towards the synthesis of an alkaloid. Great advances have been made in unravelling the constitution of the bases of the Pyridine and Picoline series, and much light has been thrown thereby on the constitution of nicotine and the Cinchona alkaloids. Moreover, important additions have been made to our knowledge of starch. It is remarkable, also, that a number of

new facts have been brought to light tending to prove that the symbolic system at present employed to represent the constitution of carbon-compounds is insufficient.

The year has not passed by without announcements of new members of the family of Elements. One of the most interesting and best authenticated is that of Scandium, which has been separated from Norwegian Gadolinite and Yttrotitanite by Neison and Cleve. I had the advantage, when last year in the University of Upsala, of being shown the spectrum of this metal by Professor Thalén, and of making the personal acquaintance of its distinguished discoverers, who showed me the enormous amount of material they worked upon in order to obtain the specimen I saw. Scandium, according to Clive, has the atomic weight 45, and the properties of its compounds are almost exactly those predicted by Mendelejeff of the hypothetical element *Ekaaboron*, to which the atomic weight 44 was assigned. We have thus apparently, for the second time, a remarkable verification of Mendelejeff's sagacity and the importance of his so-called Periodic Law. I may here refer to the service Mr. Crookes has rendered by publishing a translation of a revise of Mendelejeff's celebrated paper in *Liebig's Annalen*.

The Report of the Research Fund will be found in the Appendix, and it is not necessary for me to enter upon its details. There is much work always to be done of the highest importance to the advancement of chemistry, but which does not offer sufficient attraction to induce the devotion of the time, perseverance, and money necessary for its accomplishment; here the Research Fund steps in and removes one of the obstacles. In other cases, where the necessary zeal and talent exist to commence a valuable research, the chemist may not be in a position to devote time and money for the undertaking; but with funds at its disposal, our Society can prevent the opportunity from being lost. I trust that those whose position of fortune permits of their doing it, will contribute largely to the Research Fund, and thus promote the advancement of a science which may have contributed greatly to their own prosperity.

The Drapers' Company have for the last three years contributed £105 per annum to the Research Fund, the Goldsmiths' Company at the commencement gave a munificent donation of £1,000, the Clothworkers' Company £105, the Mercers' Company £105; the Merchant Taylors' Company £105, the Grocers' Company £100, and the Skinners' Company £52 10s. The City Companies cannot devote a portion of their vast revenues more usefully than in promoting scientific researches, for with the advance of knowledge will the prosperity of our country develope.

The past year has been one of peaceful prosperity in our Society;

and we have had a large accession to our members ; and the alteration of the bye-law relating to the election of candidates has, on the whole, worked well ; but as it has been frequently necessary to postpone the ballot for want of sufficient attendance, it has been thought desirable to make a change in it.

The following statement gives a detailed account of the access to our members, after allowing for the decrease in consequence of death and other causes :—

Number of Fellows at the Anniversary, March 31, 1879 ..	981	
Since elected, and paid admission fees	77	
		<hr/>
		1,058
Removed on account of arrears.....	10	
Deceased	14	
		<hr/>
		24
		<hr/>
		1,034
		<hr/>
Number of Foreign Members at the last Anniversary	34	
Deceased	1	
		<hr/>
		33
		<hr/>
Associate	1	

The deceased Fellows are :—Dr. G. H. Bachhoffner ; W. H. Balmain ; J. W. Bell ; R. E. Cunningham ; Dr. Edward Dowson ; Wm. Glass ; Dr. Thomas Griffith ; William Huggon ; John Mercer ; J. J. Nicholson ; Dr. William Procter ; W. Valentin ; E. P. H. Vaughan ; Thomas Wells. Foreign Member deceased :—N. Zinin.

Of some of these I have obituary notices, and hope to obtain others.

The following Fellows have withdrawn :—J. J. Bancroft ; C. C. Capel ; Rev. Robert Colman ; Dr. George Cordwent ; Alfred Colman ; Prof. Henry Croft ; E. H. Jacob ; Edward Potts ; J. Smith ; Lawrence C. T. Whitwell.

The following are the removals in consequence of the non-payment of subscriptions :—

Removals if subscriptions are not paid by March 30th, 1880 :—J. H. Atherton ; Dr. R. J. Atcherley ; J. T. Armstrong ; John Cox ; Stephen Cook ; J. McL. Glassford ; Dr. J. T. Hobson ; A. F. Hargreaves ; Dr. George Jones ; John Jones ; R. H. Kerr ; J. J. Lundy ; A. S. L. Macdonald ; John Noble ; J. C. Sellars, G. F. Thomson ; and Alfred A. Wolff.

Papers read since last Anniversary.

I. "On Terpin and Terpinol : " by W. Tilden.

- II. "On a Gold Nugget from South America:" by G. Attwood.
- III. "On Lead Tetrachloride:" by W. W. Fisher.
- IV. "On the Transformation of Aurin into Trimethyl-para-rosaniline:" by R. S. Dale and C. Schorlemmer.
- V. "On the Solution of Aluminium Hydrate by Ammonia, and a Physical Isomeride of Alumina:" by C. F. Cross.
- VI. "Researches on Dyeing. (Part II.) Note on the Emission of Colouring-matter:" by E. J. Mills and L. Campbell.
- VII. "On Heptane from *Pinus sabiniana*:" by T. E. Thorpe.
- VIII. "On the Determination of Tartaric Acid in Lees and inferior Argol, with some remarks on Filtration and Precipitation:" by B. J. Grosjean.
- IX. "Conditions affecting the Equilibrium of certain Chemical Systems:" by M. M. P. Muir.
- X. "On the Action of Aqueous Hydrochloric Acid upon Bismuthous Oxide:" by M. M. P. Muir.
- XI. "On the Action of Oxides on Salts. (Part II):" by E. J. Mills and J. W. Pratt.
- XII. "Examination of Substances by the Time Method:" by J. B. Hannay.
- XIII. "Preliminary Note on certain Compounds of Naphthalene and Benzene with Antimony Trichloride, &c.:" by Watson Smith.
- XIV. "On the Volumes of Liquids at their Boiling Points, obtainable from Unit-volumes of their Gases:" by W. Ramsay.
- XV. "On a Method of Precipitating Manganese entirely as Dioxide, and its application to the Volumetric Determination of Manganese:" by J. Pattinson.
- XVI. "On the Determination of Nitric Acid as Nitric Oxide by means of its action on Mercury:" by R. Warington.
- XVII. "On a new class of Colouring-matter:" by Otto N. Witt.
- XVIII. "On Nitrification. (Part II):" by R. Warington.
- XIX. "On the Alkaloids of the Veratrum Family. (Part III):" by C. R. A. Wright and A. P. Luff.
- XX. "On the Alkaloids of the Veratrums. (Part IV):" by C. R. A. Wright.
- XXI. "On the Alkaloids of the Aconites. (Part IV):" by C. R. A. Wright and A. P. Luff, with an Appendix by C. R. A. Wright and A. E. Menke.
- XXII. "On the action of Hydrochloric Acid on Manganese Dioxide:" by S. U. Pickering.
- XXIII. "A Preliminary Note on some Reactions of the Ammonio-Chloride of Magnesium, known as Magnesia Mixture:" by H. d'Arcy Power.

- XXIV. *The Composition of Cows' Milk in Health and Disease:*"
by A. Wynter Blyth.
- XXV. *"Notes on the Effect of Alcohol on Saliva, and on the Chemistry of Digestion:"* by W. H. Watson.
- XXVI. *"A Contribution to the Theory of Fractional Distillation:"*
by T. E. Thorpe.
- XXVII. *"Preliminary Note on the Action of Organo-Zinc Compounds on Quinones:"* by F. R. Japp.
- XXVIII. *"Third Report to the Chemical Society on Researches on some Points in Chemical Dynamics. On Curved Surfaces Expressing the Relations between Time, Temperature, and amount of Deoxidation of Copper Oxide by Hydrogen and Carbon Oxide:"* by C. R. A. Wright, A. P. Luff and E. H. Rennie.
- XXIX. *"On Fractional Distillation:"* by F. D. Brown.
- XXX. *"On Chlorostannic Acid:"* by J. W. Mallet.
- XXXI. *"On Indigopurpurin and Indirubin:"* by E. Schunck.
- XXXII. *"On Gardenin:"* by J. Stenhouse and C. E. Groves.
- XXXIII. *"On Dry Copper-Zinc Couples and Analogous Agents:"*
by J. H. Gladstone and A. Tribe.
- XXXIV. *"The Action of Sulphuric Acid on the Hydrocarbons of the Formula $C_{10}H_{16}$:"* by H. E. Armstrong and W. Tilden.
- XXXV. *"Researches on the Terpenes, Camphor, and Allied Compounds. (Part I.) On Hydrocarbons associated with the Terpenes, and on the Formation of Cymene from Terpenes and Allied Compounds:"* by H. E. Armstrong.
- XXXVI. *"On the action of Iodine on Terpenes. (Part II):"* by H. E. Armstrong.
- XXXVII. *"On Camphor Derivatives. (Part III):"* by H. E. Armstrong and M. Matthews.
- XXXVIII. *"Contributions to the History of Starch and its Transformations:"* by H. T. Brown and J. Heron.
- XXXIX. *"On the Determination of Nitric Acid by means of Indigo, with special reference to Water Analysis:"* by R. Warington.
- XL. *"Notes on the Purple of the Ancients:"* by E. Schunck.
- XLI. *"On the Heat of Formation of Aniline, Picoline, Toluidine, Lutidine, Pyridine, Dipicoline, Pyrrol, Glycerin, and Furfural:"* by W. Ramsay.
- XLII. *"On Ethylene Chlorothiocyanate and its Oxidation into Ethylene-chlorosulphonic Acid:"* by J. W. James.
- XLIII. *"On the Boiling Points of certain Metals and Metallic Salts:"* by T. Carnelley and W. Carleton Williams.
- XLIV. *"On the Transformation-products of Starch:"* by C. O'Sullivan.

- XLV. "Note on the Formulæ of the Carbohydrates:" by H. E. Armstrong.
- XLVI. "On a New Method of determining Sulphur in Coal:" by Teikichi Nakamura.
- XLVII. "On the Bromine Derivatives of β -Naphthol:" by A. J. Smith.
- XLVIII. "On the Dissociation of Ammonia-Alum:" by J. S. Thomson.
- XLIX. "On α -Methyloxysuccinic Acid, the Product of the Action of Anhydrous Hydrocyanic Acid upon Aceto-acetic Ether:" by G. H. Morris.
- L. "On the Action of Phosgene on Ammonia:" by H. J. H. Fenton.
- LI. "On the Rehydration of Dehydrated Metallic Oxides:" by C. F. Cross.
- LII. "On Alizarin-blue:" by G. Auerbach.
- LIII. "A Chemical Study of Vegetable Albinism. Part II. Respiration and Transpiration of Albino Foliage:" by A. H. Church.
- LIV. "Contributions to the History of Putrefaction. Part I:" by C. T. Kingzett.
- LV. "Notes on Manganese Dioxide:" by C. R. A. Wright and A. E. Menke.
- LVI. "On the Reaction between Sodium Thiosulphate and Iodine; Estimation of Manganese Oxides and Potassium Dichromate:" by S. Pickering.
- LVII. "On the Comparative Value of Different Methods of Fractional Distillation:" by F. D. Brown.
- LVIII. "On the Influence exerted upon the Course of certain Chemical Changes by Variations in the Amount of Water of Dilution:" by M. M. P. Muir and C. Slater.
- LIX. "On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution:" by M. M. P. Muir.
- LX. "On α - and β -Phenanthrene-carboxylic Acids:" by F. R. Japp.
- LXI. "On some Derivatives of Phenylacetic Acid:" by P. Phillips Bedson.
- LXII. "On the Specific Volume of Water of Crystallisation:" by T. E. Thorpe and J. T. Watts.
- LXIII. "Note on the Formation of Ozone during the Slow Oxidation of Phosphorus:" by H. McLeod.
- LXIV. "On the Analysis of Organic Bodies containing Nitrogen:" by W. H. Perkin.

- LXV. "On the Effects of the Growth of Plants on the Amount of Matter removed from the Soil by Rain:" by E. W. Prevost.
- LXVI. "On Dibromanthraquinone:" by W. H. Perkin.
- LXVII. "On the Melting and Boiling Points of Certain Inorganic Substances:" by T. Carnelley and W. C. Williams.
- LXVIII. "Note on the Assumed Formation of Ozone by Atmospheric Oxidation of Phosphorus:" by C. T. Kingzett.
- LXIX. "Contributions from the Laboratory of the University of Tôkiô, Japan. II. On Perthiocyanate of Silver:" by R. W. Atkinson.
- LXX. "On Methylated Dioxethylenamines:" by H. F. Morley.
- LXXI. "Note on Igasurine:" by W. A. Shenstone.
- LXXII. "On some Reactions of Tertiary Butyl Iodide:" by L. Dobbin.
- LXXIII. "On the Production of Ozone during the Combustion of Coal Gas:" by R. H. Ridout.
- LXXIV. "Some New and Improved Laboratory Appliances:" by R. H. Ridout.
- LXXV. "On River Water:" by C. M. Tidy.

Prof. Thorpe delivered a lecture "On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State."

A perusal of the foregoing list shows that the original papers are not only more numerous, but that their value has not lessened.

In the year ending 1869 we had 31 papers.

"	"	1870	"	30	"
"	"	1871	"	32	"
"	"	1872	"	22	"
"	"	1873	"	58	"
"	"	1874	"	53	"
"	"	1875	"	65	"
"	"	1876	"	66	"
"	"	1877	"	71	"
"	"	1878	"	65	"
"	"	1879	"	68	"
"	"	1880	"	75	"

Dr. GEORGE HENRY BACHHOFFNER was born April 13th, 1810, and, feeling early in life the attractions of natural philosophy and chemistry, devoted himself to the study of those sciences, on which he occasionally lectured. In 1837, recognising that the existing Adelaide Gallery did not adequately fill the scope offered for popular scientific instruction and amusement by the rapid extension of the metropolis, he invited to

his house a few influential gentlemen of similar tastes, to whom he expounded his views, and the first steps were then taken which issued, in the following year, in the opening of the Royal Polytechnic Institution. Dr. Bachhoffner was appointed Lecturer on Natural Philosophy and Electricity, and zealously fulfilled the duties of that post for the following 17 years, during which he also occasionally lectured at Eton College and elsewhere in the provinces, and in the islands of Jersey and Guernsey, in the latter of which he was made Professor of Natural Philosophy at Elizabeth College. His lectures on Armstrong's Electrical Machine, on Astronomy (delivered for several years during Lent), the Chemistry of Common Things, the Electrotpe Processes, the Manufacture of Paper, the Oxyhydrogen Microscope, and numerous other interesting subjects, were both instructive and popular. His public position involved him in extensive correspondence with inquirers on matters connected with science and its applications, and the genial interest which he took in the plans and pursuits of others obtained from them in return a large share of esteem and friendship.

Retiring from the Polytechnic in 1855, Dr. Bachhoffner became lessee, lecturer, and manager of the Royal Colosseum in the Regent's Park, which he conducted for some years with popular appreciation and success.

At the termination of his occupancy of the Colosseum, he retired into private life, retaining only his office of Superintendent Registrar of Marylebone, the long sustained strain involved in his public engagements, combined with severe domestic trouble in the loss of seven of his children, five of whom were sons, some of great promise, inducing a failing state of health which left him little desire to mingle with society. During the last years of his life he took much interest and employed much of his time in the perusal of theological literature, and, after a long illness, died July 22nd, 1879, at his house, in the Grove, Hammersmith, leaving his widow (Caroline, daughter of the eminent water-colour painter, William Derby) and two daughters.

WILLIAM HENRY BALMAIN was born on the 12th of December, 1817, in the island of Heligoland, where his father held the appointment of Staff Surgeon to the British garrison. He spent the years of his boyhood there, but the decease of his father led to his removal to London for the completion of his scholastic education. Having chosen the profession of a teacher of chemistry, he became a pupil of Dr. Edward Turner, the much esteemed Professor of Chemistry in what was then called the London University. Mr. Balmain afterwards became Dr. Turner's principal assistant, which post he occupied until the decease of that lamented Professor in 1837. Soon after that event he removed to Liverpool, where he practised as a professional chemist,

and became the teacher of chemistry at the Mechanics' Institution of that place. In 1847 Mr. Balmain removed to St. Helen's, Lancashire, and applied himself to the manufacture of various chemical products, in which he eventually became very successful, producing articles on a large manufacturing scale of a degree of purity not before attained except on the smaller laboratory scale. This remark especially applies to caustic soda, chlorate of potash, and carbonate of potash, which he manufactured at the works of the Greenbank Chemical Company, of which he was manager.

For acuteness in experimental observations, and for originality in scientific views, Mr. Balmain was very remarkable. It is, however, to be regretted that few persons outside his immediate circle had an opportunity of appreciating his talents. For some years previous to his decease he was subject to a severe affliction of the throat, and other disease of a complex character, which led him to retire from business, and to remove, in 1878, to Ventnor, Isle of Wight. Here he hoped to recruit his health, and make public some of his interesting experimental observations; but, unfortunately, the expected improvement was only partial and temporary.

In 1842 he married the daughter of Mr. Robinson, a surgeon of York. They had no children. His beloved wife died after a short illness in November last, and the intense grief he experienced at his bereavement probably hastened his own decease.

He became a Fellow of our Society in 1845, and died at Ventnor, January 15th, 1880, in the 63rd year of his age, greatly esteemed by all his acquaintance.

In 1842 Mr. Balmain published in the *Memoirs of the Chemical Society* some researches on a compound of carbon and boron, which he named *Æthogen*, capable of forming saline compounds with metallic bases. During a few of his later years he applied himself to the investigation of phosphorescent bodies, with a view to their practical application, in which he succeeded beyond all previous workers on the same subject. The phosphorescent material known as *Balmain's luminous paint*, only recently introduced, has already obtained extensive and important application; but it is to be regretted that the decease of Mr. Balmain occurred before he had completed and published his interesting observations on this subject.

Mr. JAMES WILSON BELL was the youngest son of the late Mr. Thomas Bell, Chemical Manufacturer. He was educated at the City of London School, and passing from that continued his chemical studies at the Royal College of Chemistry, then at the old house in Oxford Street, under Dr. Frankland. After passing through the usual course of practical work, he remained for a time as Assistant, and then occupied

a similar position in the Laboratory of the Royal Commission on the Pollution of Rivers for several years. On the termination of the Commission he was engaged for several years in the laboratory of Messrs. Gillman and Spencer, Consulting Brewers, chiefly in the conduct of water analysis with especial reference to the use of water in brewing.

He was never robust, and his state of health during the last three years of his life was such as to compel him to pass the winter in Algiers, and he died on September 18th, 1879, at Lower Norwood, of pulmonary consumption, at the early age of 27 years. He was an accurate and skilful manipulator, and possessed of considerable general culture. He was elected a Fellow of the Society March 4th, 1875.

Dr. EDWARD DOWSON, the son of a physician at Whitby (John Dowson, M.D., M.R.C.P.), was from boyhood an ardent student of natural history. He distinguished himself during his career at King's College, London, and soon obtained the post of Lecturer on Botany at Charing Cross Hospital.

In 1854 he went to Oxford, as demonstrator under Dr. Acland, then Lee's Reader of Anatomy at Christchurch. He zealously worked in teaching anatomy and physiology, and in the preparation of specimens, for four years. After a time he settled in London, and practised medicine. He fitted up a laboratory in his house for his brother-in-law, the late A. B. Northcote. He took great interest in chemical studies, and was himself well versed in the chemistry of physiological processes and products. His delicate health did not permit of his making a conspicuous mark in the world, but as a conscientious and exact seeker after truth, as a hearty appreciator of the work of other men, and as a painstaking and sympathetic teacher, Dr. Edward Dowson exerted a wholesome and important influence upon those with whom he came in contact. He was a pleasant companion, and a friend who endeared himself to all who knew him.

WILLIAM GLASS was born in Edinburgh on the 15th of September, 1816. When a youth of 14 he was apprenticed to a chemist and druggist in Elm Row in that city, where he remained for five years; but not liking to continue in this business he went to Professor Low, Agricultural Professor in the University there, with whom he was connected for five years. But preferring the study of chemistry he entered Dr. Read's laboratory in Edinburgh, and when that gentleman was appointed to ventilate the Houses of Parliament in London, he came up with him here, and, becoming his assistant, remained with him in that capacity for a considerable time, and while here met with the late Sir William Burnett, who at that time was prosecuting his

experiments with disinfectants, and with him, and other gentlemen who were pursuing the same course, he was connected altogether about 13 years.

Towards the end of this period of his connection with disinfectants in October, 1855, he took out a patent for "Obtaining a deodorising and disinfecting material." After this he became attached to Messrs. Hallett and Co.'s Antimony Works in Rotherhithe. During this period, in the year 1862, he took out a patent for "Improvements in the treatment of sulphuret of antimony, and in obtaining products therefrom." With this firm he remained, most assiduously applying himself to the development of their business, and only relaxing for a short period before his death, which took place on the 25th December, 1879, occasioned by disease of the heart, at the age of 63.

Mr. HUGGON was born at Leeds in 1812. He was brought up in the business of a plumber and gasfitter, and whilst so occupied evinced a strong leaning towards the study of chemistry. Mechanics' Institutes were being formed in the large towns of the north of England, and Mr. Huggon became one of the founders of that at Leeds, which has steadily advanced to a first-class institution. In 1832 Mr. Huggon and a few other members started a class for the study of chemistry upon the principle of mutual help. During the next few years he applied to the practice of dyeing the knowledge of chemistry which he had acquired. Mr. Huggon held the post of teacher of the classes in chemistry at the Leeds Mechanics' Institute for nearly 20 years, for a large part of this time giving his services gratuitously.

Mr. Huggon's life serves to mark other epochs of interest to science. In 1840 he became licensee for Yorkshire for Messrs. Pritchard and Topham's daguerreotype, and acquired a knowledge of the process by a course of training at the Polytechnic Institution, London. He practised the daguerreotype art until 1856, and in that year commenced the manufacture of photographic collodion, his products long enjoying a well-deserved commercial success.

Mr. Huggon acted as a professional analyst, and had a large practice in connection with the subjects of water, coal, iron, and dyes. Besides this, he carried on the manufacture of various chemical products used by dyers.

Mr. Huggon's kindly disposition and straightforward dealing endeared him to those who were brought in contact with him, and it may safely be said that he never made an enemy. His willingness to impart information from his large store of practical experience was especially noteworthy. After a suffering illness of two years' duration, borne with rare patience and resignation, he died at Leeds, on February 13th, 1880, aged 68 years.

Mr. JOHN MERCER was the son of the late Mr. John Mercer, J.P., F.R.S., and was born at Oakenshaw, September 3rd, 1825. In 1836 he went to Mr. George Edmonson's academy at Blackburn, and in 1841 to University College, Edinburgh, and studied there under Professors Hope, Forbes, and Jamieson in mathematics, chemistry, and physics. On leaving Edinburgh he entered the laboratory of his late father, a partner of a well-known firm of Fort, Brothers and Co., calico printers. Here he acquired so thorough a knowledge of practical chemistry and of calico-printing, that at the age 21 he took the management of the works and was admitted a partner, and continued in the business until it was given up through the illness of the senior partner. He afterwards established a cotton-spinning firm at Great Harwood, under the title of Mercer, Brother, and Co., and remained in this business for 27 years. He took a prominent part in placing Great Harwood under the Local Board Act, and was elected the first chairman, and brought about a system of effectual drainage of the town as well as the providing it with water and gas. In 1870 he was a magistrate for the county of Lancaster. Mr. Mercer was never married, but resided during their lifetime with his father and mother, and subsequently with his sisters. He died October 10th, 1879, in the 54th year of his age, after an illness of more than six months.

WILLIAM GEORGE VALENTIN was born at Neuenberg, in the Black Forest, on the 16th of May, 1829. He came to England in 1855, and, in the early days of the Royal College of Chemistry, studied under Dr. Hofmann, who subsequently made him senior assistant in the laboratory, and has recently borne graceful testimony to the esteem in which he held him.

Mr. Valentin retained the position of senior assistant under Dr. Frankland, with whom he worked in the new laboratories at South Kensington. He devised a method for the estimation of sulphur in coal gas, and being an accomplished analyst was able to render important services as chemical adviser to the Trinity House, and gas examiner to the Great Western Company. He wrote several textbooks, which possess considerable merit, and he will be long remembered as a patient and skilful teacher by the large number of the present generation of chemists, who received their practical training from him, and have reason to be grateful for his kindly interest in their success.

His devotion to teaching did not leave him time to prepare many papers for this Society, but he served on our Council and was often at our meetings. He died suddenly of apoplexy at Hastings on the 1st of May last.

Mr. THOMAS WILLS was born in Devonshire in 1850, and received his education in London at University College School and at King's College. Early in 1868 he became assistant to Professor Odling, then at St. Bartholomew's Hospital, and towards the close of the same year passed with him to the Royal Institution on his occupying the post of Fullerian Professor. Mr. Wills was elected a Fellow of the Chemical Society on February 17th, 1870, and was always a regular attendant at its meetings, contributing several papers.

In 1873 he removed to the Royal Naval College at Greenwich, where he became demonstrator of chemistry, which position he retained until his death. In 1874 the Society of Arts established a section especially devoted to chemistry, and Mr. Wills was appointed secretary, and to his energy and power of organisation must be attributed much of the success of the meetings of the section.

He was for several years one of the secretaries of Section B (chemical section) of the British Association, was one of the original Fellows of the Institute of Chemistry, and in March, 1878, was elected a member of the Physical Society.

His attention was especially devoted to the chemistry of coal gas, and for several years he was consulting chemist to the Phoenix Gas Company. He wrote many papers and delivered several lectures at various times on matters relating to gas manufacture and use, but perhaps his most important work was a short course of lectures delivered before the Society of Arts on "Explosions in Coal Mines," which were published in the Society's Journal and rewarded with the silver medal.

The excitement caused by the introduction of the electric light in the Metropolis for street lighting in the winter of 1878-9 naturally claimed his attention, and the last communication which he made to the Chemical Society was on the formation of oxides of nitrogen in the voltaic arc.

He died after only a few days' illness, of typhoid fever, on May 2nd, 1879, aged 28 years.

The following Officers were then announced from the chair as having been duly elected for the ensuing year:—

President.—Henry E. Roscoe, LL.D., F.R.S.

Vice-Presidents.—F. A. Abel, C.B., F.R.S.; Sir B. C. Brodie, F.R.S.; Warren De La Rue, D.C.L., F.R.S.; E. Frankland, D.C.L., F.R.S.; J. H. Gladstone, Ph.D., F.R.S.; A. W. Hofmann, D.C.L., F.R.S.; W. Odling, M.B., F.R.S.; Lyon Playfair, Ph.D., C.B., F.R.S.; A. W. Williamson, Ph.D., F.R.S.; J. Dewar, F.R.S.; J. H. Gilbert, Ph.D., F.R.S.; A. V. Harcourt, F.R.S.; N. S. Maskelyne, F.R.S.; R. Angus Smith, Ph.D., F.R.S.; J. Young, F.R.S.

Secretaries.—W. H. Perkin, F.R.S.; H. E. Armstrong, Ph.D. F.R.S.

Foreign Secretary.—H. Müller, Ph.D., F.R.S.

Treasurer.—W. J. Russell, Ph.D., F.R.S.

The other Members of the Council are—M. Carteighe; C. Graham, D.Sc.; C. W. Heaton; H. McLeod; E. J. Mills, D.Sc., F.R.S.; W. C. Roberts, F.R.S.; J. M. Thomson; W. Thorp; T. E. Thorpe, Ph.D., F.R.S.; J. L. W. Thudichum; W. A. Tilden, D.Sc.; R. Warington.

Dr. THE TREASURER IN ACCOUNT WITH THE CHEMICAL SOCIETY FROM MARCH 27, 1879, TO MARCH 23, 1880. Cr.

	£	s.	d.	£	s.	d.
Balance at Bank March 27th, 1879	1,963	5	1			
" in hand of Treasurer	1	4	4	1,964	9	5
Receipts by Admission Fees, Subscriptions, and Life Compositions, from March 20th, 1879, to March 18th, 1880, inclusive.						
16 Life Compositions	318	0	0			
77 Admission Fees	308	0	0			
1 Subscription for 1876	2	0	0			
10 Subscriptions for 1877	19	0	0			
44 " " 1878	84	0	0			
201 " " 1879	394	0	0			
539 " " 1880	1,626	10	6			
Sale of Journal	294	0	0	2,151	10	6
" Index	1	0	0			
Subscriptions for Proceedings of Royal Society, vols 28 and 29				295	0	9
From Society of Public Analysts	3	0	0	44	10	0
From Institute of Chemistry	8	10	0			
Dividends on Consols (£4,000)	117	10	0	11	10	0
" Metropolitan Board of Works 3½ per cent. Stock	69	8	1			
" London and North Western Railway Debenture Stock	30	17	2	217	15	3
Assets.						
Balance at Coutts'	927	17	1			
" in hands of Treasurer	2	0	3			
Three per cent. Consols	4,000	0	0			
London and North Western Railway Debenture Stock	788	0	0			
Metropolitan Board of Works 3½ per cent. Stock	2,200	0	0			
				4,684	15	11
Expenses on Account of Journal.						
Salary of the Editor	250	0	0			
" Sub-Editor	100	0	0			
Fees to Abstractors of Papers	250	19	6			
Incidental expenses of Editor	4	0	0			
Periodicals for use of Abstractors	55	8	9			
Distribution of Journal	133	7	7			
Printing of Journal	1,056	13	10	1,870	9	8
Expenses on Account of the Library.						
Salary of Librarian	50	0	0			
" Library Attendant	62	0	0			
Books and Periodicals	448	12	6			
Binding Books and Periodicals	40	19	8			
Printing Authors' Copies	601	12	2			
Royal Society's Proceedings, vols 27 and 28	42	4	0			
Reimbursing the above	118	2	8			
Reports of Meetings	4	8	9			
Miscellaneous Printing	22	10	0			
Insurance of Society's Furniture and books	33	3	2			
Stationery, Postage Envelopes, Obligation and Receipt Books	2	0	0			
Inhabited House and Income-tax	30	1	4			
Collector's Commission on Subscriptions	6	17	6			
Treasurer's Stamps and Clerical Aid	107	11	0			
	4	6	6			
House Expenses.						
Repairing and Keeping in Order Fire Hose	3	0	9			
Putting up Ventilators	10	16	4			
Cleaning and Altering Gas Fittings and Bells	9	7	3			
Providing Refreshments at Meetings	23	7	4			
Heating of Building	11	14	6			
Lighting of Building	82	4	5			
Cleaning of Building	22	4	0			
Wages of House Porter	43	8	0			
Petty House Expenses	12	18	9			
Gratuity to Gate Porter	2	2	0			
Purchase of £700 Metropolitan 3½ per cent. Stock				191	8	4
Petty Cash Disbursements	927	17	1	720	2	6
Balance in Bank	2	0	3	0	6	2
" in hands of Treasurer				929	17	4
Examined and found correct, March 23rd, 1880, { GEORGE HOGARTH MAKINS, } Auditors. { FREDERIC JAS. M. PAGE, } { ALFRED JOHN GREENSAW, }				4,684	15	11

APPENDIX.

THIRD REPORT OF THE RESEARCH FUND COMMITTEE.

DURING the past session the following sums have been granted from the Research Fund by the Council on the recommendation of the Research Fund Committee:—

£30 to Mr. M. Whitley Williams, for the elaboration of an improved method of Organic Analysis.

£25 to Mr. M. M. P. Muir, for the study of the Chemical Habitudes and Physical Constants of Bismuth Compounds.

£15 to Mr. J. M. Thomson, for experiments on the action of Isomorphous Bodies in exciting the Crystallisation of Supersaturated Solutions.

£50 to Dr. Wright, for the continuation of his investigations of certain points in Chemical Dynamics.

£25 to Mr. F. D. Brown, for the continuation of his investigation of the theory of Fractional Distillation.

£30 to Mr. Bolas, for the preparation and investigation of Alloys and Compounds of Chromium.

£20 to Dr. Japp, for the investigation of the action of the Organo-zinc Compounds on Quinones.

£100 to Dr. Armstrong, for the determination of certain physical properties, especially the Refractive Indices, of Typical Chemical Compounds.

£100 to Dr. Wright, for the determination of Chemical Affinity in terms of Electrical Magnitudes.

£100 to Mr. F. D. Brown, for the determination of the Vapour Tension of Pure Compounds and of Mixtures.

The two last-mentioned grants were made in February of this year, the others in June, 1879.

The condition of the fund is shown by the appended Balance-sheet. A donation of £105 from the Worshipful Company of Drapers, and one of £100 for which the Society is indebted to the generosity of its President, Mr. De la Rue, are important items in the income of the fund for the year. The Committee desire to point out to the Council and to the Fellows at large the desirability of obtaining further additions to the fund, for without such contributions as these the income arising from investments would be quite inadequate to meet the legitimate demands upon the fund. It is to be expected, and indeed hoped to be, that these demands will increase rather than diminish, and it is therefore especially necessary that efforts should be made to increase the income of the fund.

During the session, the results of several investigations, in aid of which grants have been made from the Research Fund, have been communicated to the Society.

Dr. TILDEN, in a paper on Terpin and Terpinol (*Trans.*, 1879, 286—290), after describing several properties of these bodies, adduces evidence to prove that the latter is a constituent of some essential oils, as oil of lemon and cajuput.

Prof. THORP has described (*Trans.*, 1879, 296—309) the results of his examination of so-called Abietene, the exudation from the Californian nut or Digger pine (*Pinus sabiniana*). He finds it to consist of the almost pure paraffin, normal heptane, C_7H_{16} , and having thus obtained a considerable quantity of this hydrocarbon, he has availed himself of the opportunity to make a series of most valuable determinations of several of its physical constants.

Dr. WRIGHT, in conjunction with Messrs. LUFF and RENNIE (*Trans.*, 1879, 475—524), has presented a voluminous third report on his researches on some points in Chemical Dynamics, describing at length the result of experiments on the relation between the rate of the reduction of cupric oxide by hydrogen or carbon monoxide, time and temperature.

Mr. F. D. BROWN has described the behaviour of mixtures of benzene and carbon bisulphide when distilled under various conditions, as a contribution to the theory of fractional distillation (*Trans.*, 1879, 547—562). In a second communication (*Trans.*, 1880, 49—60), he has embodied the results of the comparison of the value of the different methods of fractional distillation.

Drs. ARMSTRONG and TILDEN have presented an account (*Trans.*, 1879, 733—760) of their examination of the action of Sulphuric acid under various conditions on the Terpenes. One of the chief results of their investigation is to establish the fact that no such substance as terebene exists, the liquid hitherto described under this name being simply impure camphene.

Dr. BENSON (*Trans.*, 1880, 90—102) has carefully examined a number of derivatives of Phenylacetic acid, an acid which has now become of special interest to the chemist on account of its relation to indigo.

The investigation of Messrs. HARTLEY and HUNTINGTON on the action of organic compounds in absorbing the ultra-violet rays of the spectrum referred to in the last report has since been published in the Transactions of the Royal Society. These gentlemen also have since submitted to the Royal Society an account of the results of the continuation of the investigation (Proceedings, XXIX, 290).

Dr. Tilden has communicated the chief results of experiments on the action of hydrochloric acid upon terpenes—a portion of the subject

for which he received a grant from the Society—to the Chemical Society of Berlin (*Ber.*, **12**, 1311).

The experiments on the action of iodine on terpenes and on the saturated hydrocarbon referred to by Dr. Armstrong in the last report, have been partially described in communications to the Berlin Chemical Society (*Ber.*, **12**, 1756—1790). The publication of the observations on camphor has been delayed in order to render them as complete as possible.

Dr. Japp has forwarded to the Secretaries a paper which will be read at the next meeting, in which he describes the results of his investigation of the action of zinc ethyl on phenanthraquinone.

Several gentlemen who have received grants, but not yet communicated their results to the Society, viz., Messrs. Bolas, Burghardt, Dupré, Jago, Shenstone, and Williams, have favoured the Committee with preliminary reports of the progress made in their investigations.

XX.—*River Water.*

By C. MEYMOTT TIDY, M.B., M.A., M.S.

THE various conditions affecting the purity of river water, rendering it impure when pure, or pure when impure—the influence for good or for evil on the life and health of a community to which such water may be supplied for domestic purposes, filtered, and efficiently engineered, or if not supplied, as most certainly employed, by those who know no better, unfiltered and unengineered, and many other questions of a medico-chemical nature, are of such deep practical importance that I plead no apology for bringing them in some detail before the Fellows of the Chemical Society for discussion.

Moreover, the subject is one of such magnitude, that for the sake of classifying the facts I desire to bring before you, and of rendering the conclusions at which I have arrived, as far as I am able, intelligible, I propose discussing it under three distinct heads:—

1. I shall draw attention to certain analytical details of river waters.

2. I shall consider various sources of impurity to which river water is subject, and the means whereby purity is maintained by nature or may be effected by art.

3. I shall consider how far statistics warrant us in condemning or in approving the supply of river water for drinking purposes.

FIRST—I propose directing attention to certain detailed analyses of river waters.

(*α*) *River Thames.*

And first of all I will take the analyses of filtered Thames water; *first*, because it is a matter of personal interest, for we all have at times to drink it whether we like it or no, and also *first* because I suppose no water in the world has been so frequently and systematically examined.

I place before you in a table (Table Ia) the composition of the Thames water as supplied to the metropolis by the five companies that derive their supply exclusively from that source. The results stated are the averages of a very large number of experiments, and for purposes of comparison I have arranged them according to the months when the samples were collected for analysis. In this table the estimation of the total solid matter and of the hardness in columns 1 and 9 are averages of 1,200 determinations. The oxygen required to oxidise the organic matter in column 2, the nitrogen as nitrates in column 4, the lime, magnesia, chlorine, and sulphuric anhydride in columns 5,

TABLE 1A.—*Analyses of Filtered Thames Water.*

The oxygen required to oxidise the organic matter, the nitrogen as nitrates, the lime, magnesia, and sulphuric anhydride, are averages of 480 determinations made between January, 1876, and December, 1879. The organic carbon and nitrogen in column 3 are the averages of the published results of Dr. Frankland's experiments during the same period as those obtained by the oxygen process. The total solids and the hardness express averages of about 1,200 experiments.

The quantities of the several constituents are stated in grains per imperial gallon of 70,000 grains, except the organic carbon and nitrogen, which are stated in parts per 100,000.

1.	2.	3.	4.	5.	6.	7.	8.	9.	
								Before boiling.	After boiling 15 minutes.
Total solid matter.	Oxygen required to oxidise the organic matter.*	Organic C + N (as reported by Dr. Frankland to the Registrar-General).	Nitrogen as nitrates and nitrites.	Lime (CaO).	Magnesia (MgO).	Chlorine.	Sulphuric anhydride.	Hardness.	
grains.	grain.	part per 100,000.	grain.	grains.	grain.	grains.	grains.	degrees.	degrees.
January	0.0890	0.344	0.1471	8.192	0.480	0.926	1.708	14.14	3.90
February	0.0592	0.249	0.1067	8.738	0.494	1.013	1.616	14.12	3.74
March	0.0701	0.268	0.1453	8.532	0.578	1.021	1.792	14.28	3.54
April	0.0688	0.246	0.1238	8.068	0.470	1.168	1.638	13.73	3.30
May	0.0614	0.212	0.1306	8.084	0.526	1.031	1.664	13.72	3.39
June	0.0746	0.237	0.1228	7.638	0.502	1.036	1.638	12.86	3.21
July	0.0732	0.218	0.1054	6.890	0.505	1.018	1.340	13.39	3.06
August	0.0640	0.199	0.1054	7.754	0.553	1.012	1.170	13.52	3.27
September	0.0867	0.225	0.1091	7.917	0.441	0.965	1.241	13.54	3.26
October	0.0658	0.204	0.1262	7.971	0.428	0.965	1.402	13.76	3.53
November	0.0486	0.192	0.1178	8.028	0.486	0.951	1.302	14.30	3.62
December	0.0801	0.283	0.1185	7.701	0.513	0.927	1.656	13.93	4.25

* The oxygen required to oxidise the organic matter is determined by a standard solution of potassium permanganate acting for three hours.

6, 7, and 8 express averages of 480 experimental determinations made between January, 1876, and December, 1879. In column 3 I have given the averages of the organic carbon and nitrogen as determined by Dr. Frankland, and published in the reports of the Registrar-General, during the same period as the tabulated results by the oxygen process were obtained.

* I may here mention once for all that in this and in all cases I have expressed results in grains per gallon, except the quantities of organic carbon and nitrogen, which are throughout stated in parts per 100,000.

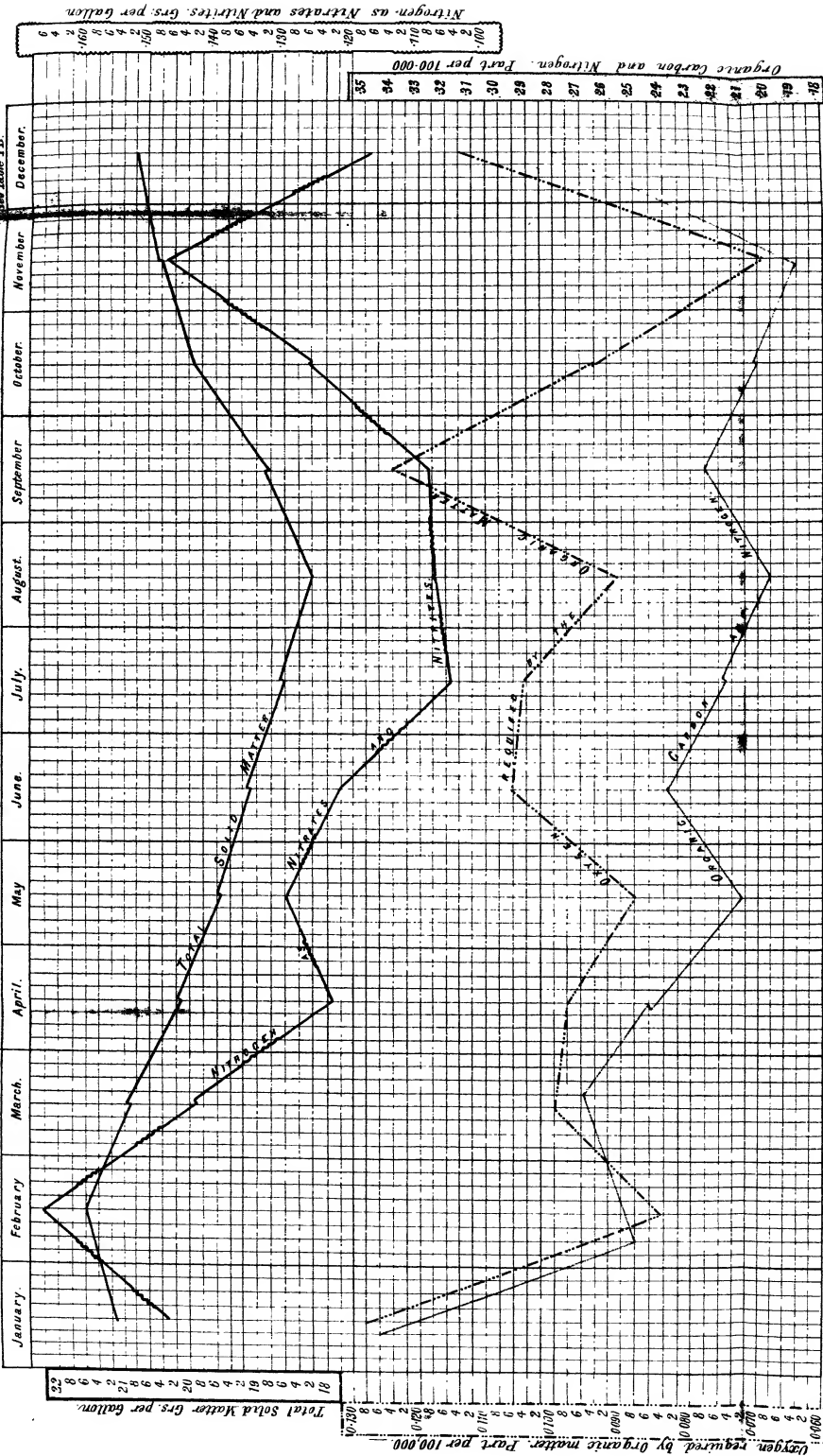
These numbers exhibit a remarkable sequence and one that is worth noting in detail.

Regarding the *total solid matter* in Thames water, I would remark that the results exhibit a complete wave (so to speak), and in their order an unbroken wave-line in the course of the year. This is best seen by means of a wave diagram (Table Ib). Beginning at February, where the highest point of the wave (or the crest as it is called) occurs, it will be remarked how it descends for six months, month by month, with perfect regularity to August, in which month we find the furrow of the wave, from which point it rises month by month for six months, and again with perfect regularity, to February. The average total solid matter in February (that is, where the *highest* point of the wave is found) is 21·634 grains per gallon, whilst in August (that is, where the *lowest* point of the wave occurs) the total solid matter is 18·240 grains per gallon. It would thus appear that the *average* variation of the solid matter in Thames water is only 3·394 grains per gallon, that is, an increase or decrease of about half a grain more or less per month. I say the *average* variation, because of course the *absolute* variation is considerably greater than this. Thus I have found the total solid matter in filtered Thames water to be as low as 16 grains per gallon, whilst I have also found it to be as high as 23·0 grains. Both of these numbers, however, express very exceptional results in opposite directions. I think from 17 to 22 grains, or a difference of 5 grains per gallon, may be taken to express more accurately the absolute variation of the solid matter in filtered Thames water.

In column 9 I have stated month by month the hardness of the water before and after boiling for fifteen minutes. The average range of the initial hardness is from 12·8° to 14·3°, and this very nearly expresses the absolute range as well. The hardness after boiling (which after all is not of the practical value we once supposed it) ranges as an average from 3·0° to 4·2°. Speaking generally it may be said that the hardness of Thames water is diminished by efficient boiling to less than one-third its initial hardness. But to effect this diminution the boiling must be efficient.

DIAGRAM SHEWING THE COMPOSITION OF FILTERED THAMES WATER.

Table I.B.



Total Solid Matter Grs. per Gallon.

Oxygen required by Organic matter. Part per 100,000.

In columns 5, 6, and 8, I have given the averages of the results I have obtained of monthly determinations of the lime, magnesia, and sulphuric anhydride during several years. I place them on record now, although I have very little to note at present with reference to them. I believe this is the first time that determinations of these constituents, extending over a long period, have been made regularly in the case of any single water. I do not propose in future to continue these determinations, which have occupied a great deal of time, and I leave them now to tell their own story.

In column 7 will be found recorded the monthly averages of the chlorine found in the Thames water. It is to be noted that from September to January—that is, during and within the period when the wave-line is rising, the chlorine is under one grain per gallon, whilst from February to August inclusive—that is, during the period when the wave-line is falling, including those months where the wave has reached its highest and its lowest points, the chlorine exceeds one grain per gallon. It is tempting to speculate on the cause of this, but I prefer for the moment to leave the facts to speak for themselves.

In column 2 I have stated month by month the average organic purity of Thames water as indicated by the oxygen process, that is, by the quantity of oxygen used up by the organic matter, determined by a standard solution of potassic permanganate acting for three hours, which process I described in some detail in a former communication. The *average* amount of oxygen required ranged from 0.089 grain per gallon to 0.048. Here again I must note that the actual limits are very much wider than these numbers represent. Thus I have known filtered Thames water require as little as 0.01 grain per gallon of oxygen and as much as 0.2 grain of oxygen (or 20 times as much as the minimum) to oxidise the organic matter. These were I need not say very exceptional results, the one exceptionally high and the other exceptionally low. From 0.03 to 0.1 grain of oxygen per gallon may be taken as the ordinary absolute limits of variation.

It is interesting to note that the quantity of total solid matter in the water is in no respects a gauge of its organic purity as judged by the quantity of oxygen required. Thus the two months when the oxygen required was greatest were respectively the month preceding the greatest quantity, and the month succeeding the smallest quantity, of solid matter in the water. Further, in February, when the solid matter is at its maximum, the oxygen used up by the organic matter was almost at its minimum. Much of all this depends on certain exceptional circumstances, some of which we shall discuss hereafter, but this I may add here, that the term “total solid impurity” to express the “total solid matter” in water, is scarcely expressive of the facts,

and its use, although chemically accurate, may lead to some misapprehension.

In column 3 I have stated the average monthly quantities of organic carbon and nitrogen for the four years 1876—1879 inclusive, as reported by Dr. Frankland, this period corresponding to that comprehended in column 2, where the results by the oxygen process are tabulated. The results so far are comparable, because the examinations were in both cases conducted on samples of Thames water taken always within a day or two of each other, although I regret to say they were not conducted on identical samples. The results are better seen and compared by reference to the wave diagram. I would remark that whatever variations occur the results in no one case transgress the comparison classification I ventured to place before you on a former occasion. The agreement in the testimony afforded by these two processes is remarkable. I have no desire to repeat what I have already said on this subject, but I shall be pardoned for taking this opportunity of placing these comparison results before you, in order to confirm by a different course of reasoning, and by a rearrangement of facts, what I have I am bold enough to say proved in my previous communication to the Society (well, I will be modest, and say proved to my own satisfaction). In such an exceptional case as water analysis, where we can have no absolute knowledge of what the exact nature or constitution of the organic matter present in solution is (or perhaps I ought to say organic matters, for their variety in a single water may be numberless), concurrence of testimony, by which I mean the same story told by two or more absolutely independent experimental witnesses, is, if not the only means, at any rate the chief means of proving the exact value to be attached to the results obtained by any given process. For whilst the oxygen process only records the oxygen used by a part of the organic matter, the combustion process only records the organic carbon and nitrogen in the residue, no estimation being made of the organic carbon and nitrogen lost or dissipated during the evaporation. This, I take it, is the position of the oxygen and combustion processes—both are comparative—prove the one right, you prove both right; prove one fallacious, and both must fall. I shall not again refer to this question, and I shall be excused therefore expressing regret here that conclusions of grave importance sanitarily, and involving serious interests monetarily, should ever be based on determinations of the so-called albuminoid ammonia, which determinations are as incapable of arrangement or of interpretation as they are outside the sphere of scientific accuracy.

In column 4 I have given the monthly averages of the nitrogen as nitrates and nitrites. The results are curious when regarded side by

side with the organic matter. Speaking generally, there is a certain want of accord to be noted.

Thus, from January to February, from April to May, from September to October, and from October to November, there are falls in the quantity of organic matter in the water, whilst in each case a rise in the amount of nitrogen as nitric acid is recorded. Conversely, from February to March, from May to June, and from November to December, the organic matter shows a rise, and the mineral nitrogen a fall. These are the facts. It may be that the organic nitrogen of one month becomes the inorganic nitrogen of the next, and the results somewhat confirm this view. At the same time it is worth noting that there is a very manifest relationship between the total solid matter in the water and the nitrogen as nitric acid, and this of itself may be sufficient to explain the various quantities found. Practically, however, the variations are of little consequence.

I have estimated the dissolved gases in filtered Thames water on 27 different occasions. Of these examinations, 17 were made on the water collected during the summer months (that is, from May to October inclusive), and 10 during the winter months (that is, from November to April inclusive). I shall content myself with merely recording the average results of the 27 experiments and the averages of the summer and winter determinations respectively (Table II). The only point worth remarking, is that the oxygen in solution during the winter months was found to be very nearly double the amount held in solution during the summer months, or exactly 2.19 cubic inches per gallon in the winter against 1.19 cubic inches in the summer. I mention this because it is noteworthy that the least oxygen is present during the months of the greatest organic purity. I admit, speaking generally, that I have not yet been able to make very much myself of the estimation of the dissolved gases as an indication of the purity or impurity of a water; but my experience in this matter is limited. I cannot help thinking, however, that it would be well worth while in every case to estimate the dissolved oxygen. If the water was found to be saturated, it would certainly, one would have thought, indicate freedom from oxidisable organic or other matters, and therefore a strong *à priori* argument in favour of purity, and *vice versâ*. But this remains to be proved. I regret that more has not been done in this direction, and I intend in future to turn my attention to this far too neglected point in water analysis.

TABLE II.—*Dissolved Gases present in Filtered Thames Water.*

Cubic inches in one imperial gallon of water.	Average of 27 analyses.	Average of 17 analyses during the summer months (May to October).	Average of 10 analyses during the winter months (November to April).
	Cubic inches.	Cubic inches.	Cubic inches.
Oxygen	1·69	1·19	2·19
Nitrogen	3·71	3·61	3·81
Carbonic anhydride....	11·55	11·70	11·40
Total	16·95	16·50	17·00

I have given in Table III the average results of monthly analyses of the unfiltered Thames water taken during the past six years. The samples were collected in mid-river at Hampton on or about the 15th of each month. The analysis was conducted on the water as delivered, that is, without time having been allowed for the matters in suspension to subside. The sequence in the quantity of total solid matter is not so perfect in this set of experiments as in those on the filtered water, depending no doubt on the different quantities of suspended matter in the river at different times, although, speaking generally, the one set of experiments confirms the other. I might mention here that the solid matter in suspension rarely exceeds 1 grain per gallon, from 0·4 to 0·7 being the quantity ordinarily found. If the river contains 1 grain of suspended matter per gallon, it appears very turbid indeed when seen in the two-foot tube, whilst 1·5 grains would render it pea soupy in the extreme, and so thick in the two-foot tube that it would be impossible to read writing through it, or even in some cases to distinguish the black lines at all.

(β) *River Lea.*

In Table IV I place before you the average of monthly analyses of the water of the River Lea. I ought to state, however, that in reality the results relate to the water supplied to their district by the East London Water Company. I mention this because this company possess Parliamentary powers to take a certain limited quantity of water from the Thames, and of these powers they occasionally avail themselves. Thus I find between 1877 and 1879 they did so on several occasions, but the quantity thus abstracted from the Thames was only $\frac{1}{7}$ th of the total supply. I don't think this can materially affect the results.

TABLE III.—*Analyses of Unfiltered Thames Water.*

These results express averages of 72 experiments conducted during the years 1874—1879 inclusive. The samples were taken at Hampton, opposite the works of the West Middlesex Water Company, in the middle of each month, and about 1 foot below the surface at mid-river.

The results are stated in grains per imperial gallon.

	1. Total solid matter.	2. Oxygen required to oxidise the organic matter.	3. Nitrogen as nitrates and nitrites.	4. Lime (CaO).	5. Magnesia (MgO).	6. Chlorine.	7. Sulphuric anhydride.	8. Hardness.	
								Before boiling.	After boiling 15 minutes.
January	grains. 21·920	grain. 0·1216	grain. 0·1568	grains. 8·190	grain. 0·024	grains. 0·907	grains. 1·775	degrees. 14·64	degrees. 4·02
February	21·574	0·0920	0·1574	8·138	0·558	0·981	1·574	14·18	3·92
March	21·427	0·0982	0·1457	8·474	0·518	0·949	1·553	14·77	4·10
April	19·894	0·1025	0·1312	8·003	0·504	0·967	1·526	14·05	3·62
May	18·945	0·0638	0·1376	8·173	0·504	1·015	1·607	13·84	3·65
June	19·062	0·0787	0·1250	8·238	0·517	1·031	1·443	14·10	3·88
July	18·534	0·1034	0·1068	7·115	0·528	1·024	1·210	13·64	3·01
August	18·913	0·1073	0·1127	8·326	0·432	1·030	1·092	14·20	3·30
September	17·778	0·1104	0·1104	8·384	0·431	0·975	1·387	14·30	3·34
October	19·732	0·0854	0·1430	7·865	0·528	0·954	1·341	14·46	3·30
November	21·196	0·1292	0·1442	8·603	0·540	0·990	1·311	14·86	3·94
December	22·020	0·1064	0·1394	8·023	0·503	0·943	1·620	15·35	4·24

TABLE IV.—*Analyses of Filtered River Lea Water.*

The results in the table express averages, in the case of the lime, magnesia, chlorine, and sulphuric anhydride, of 72 experiments conducted during the years 1877—1879 inclusive. The total solid matter and the hardness express averages of 240 experiments conducted during the ten years 1870—1879 inclusive. The oxygen required to oxidise the organic matter in column 2, and the organic carbon and nitrogen in column 3, are the results of experiments conducted during 1877, 1878, and 1879, and are strictly comparable.

The results (except the organic C and N) are stated in grains per imperial gallon.

1. Total solid matter.	2. Oxygen required to oxidise the organic matter.	3. Organic C + N (as re- ported by Dr. Frank- land to the Registrar- General).	4. Nitrogen as nitrates and nitrites.	5. Lime (CaO).	6. Magnesia (MgO).	7. Chlorine.	8. Sulphuric anhydride.	9. Hardness.	
								Before boiling.	After boil- ing for 15 minutes.
		part per 100,000.	grain.	grains.	grain.	grains.	grains.	degrees.	degrees.
January	grain. 0·0668	0·298	0·110	8·388	0·623	0·984	1·869	14·91	4·03
February	0·063	0·268	0·166	9·281	0·531	1·176	1·958	15·90	4·38
March	0·056	0·225	0·128	9·058	0·789	1·150	2·141	14·82	4·20
April	0·038	0·165	0·155	8·223	0·528	1·119	1·890	13·91	3·40
May	0·048	0·170	0·141	7·887	0·658	1·140	1·985	13·27	3·87
June	0·047	0·224	0·120	7·554	0·615	1·104	1·713	13·00	3·40
July	0·054	0·227	0·095	7·132	0·565	1·119	1·398	13·40	3·33
August	0·061	0·199	0·101	7·658	0·582	1·083	1·337	13·58	3·99
September	0·051	0·186	0·100	6·160	0·425	1·095	1·514	13·08	3·40
October	0·048	0·156	0·120	7·875	0·468	1·069	1·393	13·73	3·67
November	0·030	0·191	0·120	7·794	0·495	1·069	1·133	14·55	3·66
December	0·057	0·228	0·132	7·470	0·573	1·045	1·298	13·40	4·3

The total solid matter and the hardness in columns 1 and 9 express averages of 240 experiments conducted during the years 1870 to 1879 inclusive. In the case of the other constituents, viz., the lime, magnesia, sulphuric acid, chlorine, nitrogen as nitrates, and the oxygen required, they are averages of 72 experiments made between 1877 and 1879 inclusive. To these I have added in column 3 Dr. Frankland's returns of the organic carbon and nitrogen during the same period, for purposes of comparison with the results obtained by the oxygen process.

And again in the River Lea, as in the main river, regarding the total solid constituents of the water, we find a complete wave in the course of the twelve months, and an unbroken wave-line. February again, as in the Thames, occupies the crest of the wave, for here the maximum total solid matter was recorded (viz., 23·343 grains per gallon), whilst September occupies the furrow of the wave with the minimum total solid matter (viz., 17·993 grains per gallon). But there is a point here to be specially noted, that whereas in the Thames the average variation was only 3·394 grains per gallon, that is, the distance between crest and furrow was between 18·240 and 21·634 grains, in the Lea the average variation is as much as 5·350 grains (or more than half as much again), the range of the wave-line being between 17·993 and 23·343 grains. It is clear therefore that in this respect the Lea is less constant than the Thames, the solid matter at times being in excess of what is to be found in the main river.

The chlorine in the River Lea is slightly in excess of the chlorine in the Thames.

I would again direct attention to the columns where the results by the oxygen and combustion processes are recorded, to show the remarkable correspondence of their story. It is, moreover, worth noting that both sets of results, when compared with the analyses of the Thames water previously referred to, clearly indicate that so far as organic purity is concerned, the River Lea is slightly purer than the main river.

I do not think there are any other points in the table I need discuss in detail.

(γ.) *River Nile.*

In Table V I place before you analyses of monthly samples of the water of the River Nile taken at Cairo during one entire year. Of course the observations of one year lack the accuracy of a series of experiments conducted over several years, such as I have recorded in the case of the River Thames, where possible experimental errors and exceptional occurrences are compensated for by number. Yet these results are, I think, of sufficient importance to justify me in submitting

TABLE V.—*River Nile.*

	Matters in Solution.										Matters in Suspension.		
	Total solid matter.	Ammonia.	Nitrogen as Nitrates.	Oxygen required to oxidise the organic matter.	Lime (CaO).	Magnesia (MgO).	Sulphuric anhydride (SO ₂).	Chlorine = common salt. Cl = NaCl.	Hardness.		Organic.	Mineral.	Total.
									Before boiling.	After boiling.			
	grains.	grain.	grain.	grain.	grains.	grain.	grains.	grs.	degrees.	degrees.	grains.	grains.	grains.
January	10.13	0.006	trace	0.112	3.21	0.325	1.38	0.169 = 0.28	6.5	2.0	1.34	10.38	11.72
February	10.27	0.004	trace	0.139	2.83	0.712	1.25	0.175 = 0.29	6.5	2.0	turbid	—	—
March	12.47	0.002	trace	0.182	4.35	0.723	1.42	0.430 = 0.71	7.0	2.4	turbid	—	—
April	12.73	0.003	trace	0.246	3.32	0.757	1.78	0.640 = 1.06	8.0	2.8	turbid	—	—
May	14.33	0.001	trace	0.274	3.53	1.088	1.77	1.230 = 2.02	8.0	2.4	slightly turbid	—	—
June	14.21	0.004	trace	0.129	2.919	0.766	1.84	1.395 = 2.30	6.0	1.6	0.58	4.26	4.84
July	11.47	0.009	trace	0.092	2.788	0.913	1.84	0.714 = 1.18	5.6	1.6	6.11	6.11	12.49
August	11.62	0.003	trace	0.104	3.072	0.688	1.19	0.509 = 0.64	5.9	2.0	12.89	91.52	104.41
September	13.61	0.006	trace	0.169	2.964	0.412	1.36	0.175 = 0.29	5.0	1.2	4.14	33.84	37.98
October	11.10	0.005	trace	0.211	2.048	0.337	1.31	0.412 = 0.68	6.0	2.0	3.21	23.25	26.46
November	10.47	0.005	trace	0.118	3.00	0.595	1.31	0.145 = 0.24	6.5	2.0	2.58	21.48	24.06
December	9.53	0.003	trace	0.081	2.97	0.485	1.19	0.194 = 0.32	6.5	2.4	1.36	18.88	20.24

them to you, more especially as I am not aware of a series of analyses even as complete as this recorded concerning this interesting river.

The results are remarkable. Regarding them as a whole, the total solid matter ranged from 9·5 grains to 14·3 grains per gallon, the initial hardness varying from 5° to 8° on Clarke's scale. On each occasion a trace, but a trace only, of nitrogen as nitric or nitrous acid was recorded. The quantity of chlorine was exceedingly inconstant, varying from 0·145 grain per gallon to 1·395 grain. The organic purity of the river as estimated by the oxygen process was also subject to marked variation, the oxygen used ranging from 0·081 grain to 0·274 grain per gallon.

All the samples were turbid, and many thick (or pea-soupy, as it is called), excepting the water collected in May, which is only noted as being slightly turbid. The quantity of total suspended matter, and the relative amounts therein of mineral and organic matter in those cases where the quantity was sufficient to allow of its estimation, are duly recorded in the table.

But the results of these monthly analyses of the River Nile deserve more than general remark, because they bring before us on so much grander a scale than in the case of any river in this country, one cause of varying quality inseparable more or less from all river water, viz., the influence of flood. I shall discuss hereafter the practical bearing of this subject, but I would note here in how marked a manner the chemical purity, turbidity, and other conditions of a river water are influenced by the presence, or the absence, or (what is even more material still) the exact period of the presence or the absence, of flood. It is worth our while to note further how practically impossible it is from any single examination of a river water to decide its character or its value. To know a river thoroughly, you must know it in all states and conditions.

During April, May, and June, the Nile is at its lowest level. The details of the analyses show, as we should expect, considering the absence of rain and that the swamps in the upper part of the river are draining off, that during these three months the water (speaking generally) is at its worst. The solid matter ranges from 12·73 to 14·33 grains per gallon, the chlorine from 0·640 to 1·395, whilst the initial hardness in the samples examined during two of these months, reached its maximum of 8°. Examined by the oxygen process, the water required from 0·129 grain to 0·274 grain of oxygen per gallon to oxidise the organic matters present. The matters in suspension, however, during these three months were comparatively small in quantity, the water being recorded as turbid in April, slightly turbid in May (in neither of which months was the actual quantity of suspended matter estimated, because of the insignificant amount), whilst

in June, 4.84 grains per gallon of suspended matter was obtained, of which about one-eighth only was organic. I may mention here that the whole of the water during this period may be regarded as due to the drainage area of the White Nile and the great lakes south of the equator.

Of the three months, April, May, and June, to which I am referring, the Nile is lower in May than in any other month, and it is in the May sample that we find the maximum solid matter, the maximum organic impurity, nearly the maximum chlorine, and the maximum hardness; but the sample is the only one of the twelve which is noted as "only slightly" turbid. It may be worth remarking that in May the quantity of magnesia found was unusually large, almost ten times as much as that recorded in some of the other months.

The month of July is the only true transition month from low to high water in the case of the Nile, and at this season, owing to the floods coming down from the Atbara (a feeder which joins the Nile about 1,400 miles by river from the Mediterranean, and has its rise in the Abyssinian mountains), the river rapidly rises. In July the red mud, characteristic of the Blue Nile, begins to show itself. The suspended matter is then found to be 12.49 grains per gallon, but the total dissolved matter decreased from 14.2 grains, as recorded in the June sample, to 11.4 grains, the chlorine being very little more than one-half the amount found in the previous month. From the end of July or the commencement of August to the end of the month, the swelling of the river proceeds with enormous strides, reaching its state of maximum flood during the first few days of September. From this date, throughout the whole of September and the whole of October, the condition of maximum flood persists. The August sample was in most respects chemically like that collected in July, the two noteworthy points of dissimilarity being a slight reduction in the quantity of chlorine and an enormous increase of the matters in suspension, no less than 104.41 grains per gallon, of which 91.52 grains was mineral, being recorded. From quite the end of October, the rains having ceased and the floods being over in the upper part of the river, through November, December, January, February, and March, the river gradually falls, the disappearance of flood being very much slower but more regular than its appearance. The rise from low to high water occupies about six weeks, but the fall from high to low water occupies almost as many months. It is within the period of fall that practically we find the best water. Thus in December, when the fall is very regular and the river as nearly as possible midway between the extremes of maximum flood and extreme fall, we find the solid dissolved matters reach their minimum of 9.5 grains per gallon, the chlorine being less than 0.2 grain, whilst the oxygen required to

oxidise the organic matter is less than one-third of that used up by water at the period of its lowest level. We may perhaps regard this as the most natural state of Nile water; in other words, the river water as little influenced by interfering conditions as any. As regards turbidity we found that the suspended matter decreased rapidly from August, when the turbidity was at its worst, to February, when the quantity was so small as not to be worth determining quantitatively.

TABLE VI.—*Average Heights in Metres of the Nile at the Barrage, at 5-day intervals, for the years 1846—61.*

	5	10	15	20	25	28--31
January.....	2·79	2·68	2·58	2·48	2·39	2·26
February.....	2·18	2·07	1·96	1·83	1·72	1·65
March.....	1·54	1·45	1·35	1·26	1·18	1·08
April.....	0·99	0·94	0·87	0·81	0·74	0·69
May.....	0·61	0·62	0·58	0·53	0·51	0·47
June.....	0·14	0·18	0·18	0·48	0·66	0·76
July.....	0·90	1·05	1·27	1·44	2·16	3·22
August.....	4·15	4·87	5·57	5·76	5·87	5·97
September.....	6·09	6·13	6·18	6·17	6·19	6·48
October.....	6·60	6·55	6·51	6·37	6·21	6·22
November.....	5·73	4·97	4·66	4·09	4·00	3·80
December.....	3·61	3·12	3·25	3·19	2·97	2·90

Between 1825 and 1874 the lowest high Nile was 5·80 metres and the highest high Nile 8·48.

I desire here to express to Professor Ansted, and to Mr. John Dixon, C.E. (to whom I am indebted for Table VI, showing the average height of the Nile at five-days' intervals for the years 1846 to 1861), my obligations for much information on the state of the river at different periods of the year. There is scarcely any river in the world, and certainly there is no first-class river, where the drainage system is so simple and directly connected with the quality of the waters as the Nile. It has remarkably few tributaries, and these hardly modify the conditions of the flow except as regards the Blue Nile. It is because of the clear, precise, and easily traced relationship between the condition of the water and the condition of the river and its flow, that I must apologise for having transgressed a little the bounds of pure chemistry.

I shall content myself with placing before the Society at this point certain analyses of two other rivers only, viz., the Severn and the Shannon. The statement of the results differ from those I have already noted in that the samples examined (all of which I collected myself) were taken on the same day at different spots extending over a considerable run of river. I have chosen these two rivers for a

definite reason. In the case of the Severn the samples were collected along the river course, extending from above Worcester to Tewkesbury (a distance of about 16 miles), the sewage of Worcester on the day and at the time the samples were taken being discharged into the river. This, therefore, may be taken to be what has been called a sewage or animal-polluted river. I should have preferred (and it would have answered my purpose better) to have taken a sewage-polluted river more free than the Severn from peaty matter; and some allowance must therefore be made for the vegetable matter present in the water in rather large quantity.

The case of the Shannon is different. Practically it receives no sewage or animal pollution at all, the population of its banks for a distance of the 40 miles covered by the analyses being, as I can personally testify, comparatively nil. But with vegetable matter the river abounds, receiving as it does the drainage of the very extensive peat bogs peculiar to the country. It may therefore be taken as a good example, indeed the best possible example, of a river where the contamination is entirely vegetable.

(c.) *River Severn.*

The analyses I submit to you of the River Severn were conducted on samples collected by Professor Ansted and myself in January, 1878, at various spots from Worcester, above the sewage outfall, down to Tewkesbury, a distance by river of 16 miles. In the course of this river the Teme joins the main river. This being the largest feeder of the Severn, and bringing down a great body of very pure water (the river being celebrated for the excellence of its fish), I have thought it desirable to insert the results of the examination of the water, more especially considering the manifest influence it exerts on the composition and characters of the main river. I may add that on the day the samples were collected the river was 18 inches above mean ordinary level, and the water had a mean temperature of 7.5° C.

At Worcester the Severn may be considered to have attained a definite character, having flowed at that spot about 180 miles from the Welsh mountains, with little population near its banks except at Shrewsbury.

I shall not at this moment enlarge further on the results of the analyses stated in the tables, as I propose referring to them later when I discuss the question of oxidation in running water. I content myself now with remarking that it would appear that in the month when the samples were collected the Severn contained about 16 grains of solid matter per gallon, of which the chlorine is nearly double what it is in Thames water (owing to geological conditions), whilst the initial hardness is some 3° less.

There is one peculiarity I have noted in the River Severn and which I wish to record, never having met with it, at any rate in so well-marked a degree in any other river, and that is a very considerable increase at certain spots in the quantity of chlorine. I could myself undertake to collect two samples of water at places in the river not more than a quarter of a mile distant, there being no possible source of sewage contamination, so far as one could judge, between the two spots selected, where the chlorine of the one sample should be exactly double the chlorine of the other, the increase being unaccompanied by any corresponding increase either in the quantity of the organic matter or of the nitrates. I have been enabled to verify this fact on three distinct occasions at the same spots. My friend, Professor Ansted, who was associated with me on one of those inspections, considers that the existence of bottom springs rising through the new red sandstone (itself a salt-bearing stratum) is the explanation of this unusual occurrence, the possibility of which in river investigations it is most desirable should not be lost sight of. He informs me that salt springs are also well known to rise in the bed of the Trent, and affect the quality of the river water in a very sensible degree.

(ξ.) *River Shannon.*

The specimens of Shannon water, the detailed analyses of which are stated in Table VIII, were collected by Mr. Mylne and myself in October, 1879, the river being at the time some 2 feet above ordinary summer level. I may remark that I have selected this river (1) because it drains a larger area than any single river of the British Islands; (2) because, whilst for all practical purposes it is absolutely uncontaminated with animal impurity, it contains a large quantity of dissolved vegetable or peaty matter; and (3) because it supplies us with an excellent illustration of what may be regarded as a typical peculiarity of the Irish rivers, viz., the intervening lakes whereby the flood water is prevented for a time from running off into the sea. I may add that the analyses in the table include samples taken at the extreme ends of one of these lakes (the Lough Derg) into which the river expands.

Portumna (the village itself being situated about one mile from the river) is at the north of the Lough Derg, a lake 25 miles long formed by the expanse of the Shannon. Here the first sample was taken, and its mere appearance in a tumbler showed a superabundance of peat. The second sample was taken at the south of Lough Derg, 25 miles from where the first specimen was collected. Between Killaloe and about $1\frac{1}{2}$ miles above the town of Limerick, a distance by river of about 16 miles, several samples were collected. I shall refer to these

TABLE VIII.—*Analysis of the Water of the River Shannon (August 25th, 1879).*

The constituents are stated in grains per gallon, except the organic carbon and nitrogen, which are stated in parts per 100,000.

	Total solid matter.	Ammonia.	Nitrogen as nitrates and nitrites.	Oxygen required to oxidise the organic matter.	Organic carbon.		Organic nitrogen.	Lime (CaO).	Magnesia (MgO).	Chlorine = common salt.	Sulphuric anhydride (SO ₂).	Hardness.	
					part per 100,000	grains.						Before boiling.	After boiling.
River at Portumna (north of Lough Derg).	grains. 17·10	grain. 0·002	grain. mere trace.	grain. 0·332	0·950	100,000 0·040	grains. 7·28	grains. 0·792	grains. 1·008	grains. 1·652	grains. 0·70	degrees. 12·5	degrees. 4·7
River at Killaloe (south of Lough Derg).	15·30	0·001	"	0·284	0·800	0·040	6·10	0·790	1·008	1·652	1·04	11·5	4·2
River one mile below Killaloe.	16·80	0·008	"	0·216	0·480	0·036	6·60	1·081	1·08	1·77	1·07	11·6	3·5
River at O'Brien's bridge ..	17·30	0·001	"	0·284	0·840	0·060	6·72	0·936	1·008	1·652	0·93	11·5	4·2
" one mile below Castle Connell.	20·20	0·008	"	0·223	0·593	0·050	5·82	0·720	1·008	1·652	0·87	11·1	4·0
River above the junction of River Mulcaire.	18·90	0·001	"	0·373	0·914	0·070	6·71	0·792	1·08	1·77	0·80	12·2	4·5
River a quarter of a mile below the junction of the River Mulcaire.	17·90	0·001	"	0·270	0·610	0·060	6·72	0·756	1·008	1·652	0·80	10·5	4·7
River at Limerick	17·20	0·001	"	0·221	0·431	0·040	6·16	1·081	1·008	1·652	1·04	9·5	4·5

analyses hereafter in connection with peaty contamination (with which the river abounds to a far greater extent than in any English river), and I here only draw attention to the following general facts:— (1) that the solid matter in different parts of the river flow ranged from 15·3 to 20·2 grains; (2) that in no case was there found more than a mere trace of nitrogen as nitric acid, whilst (3) the chlorine was remarkably constant at 1·0 grain per gallon.

SECOND.—*The various sources of impurity to which river water is subject, and the means whereby purity is maintained by nature, or may be effected by art.*

In dealing with this part of my subject I shall be compelled to limit myself to three sources of impurity—(1) the *influence of flood water on the general purity of the river*; (2) *peaty or vegetable contamination*, and (3) *sewage or animal contamination*. It was at one time my intention to have considered the pollution of river water by the refuse of various trade and manufacturing operations, and to have examined the various circumstances that influence the nature and amount of the mineral constituents. These latter, except in the case of the influence exerted by geological formations, have as yet received very insufficient attention. I found, however, that these questions involved considerations of such extent that I am compelled to reserve them for the present.

(1.) *Flood Water.*

By “a flood” is implied a swollen river, and as a result (and this is most important) an increased velocity of the river flow. A more or less heavy flood indicates a more or less heavy rainfall over the whole or a part of the drainage area. Confining our attention to the influence of flood on the condition of the river water, we need scarcely regard the rain that falls directly into the river. No doubt this may fractionally increase the purity of the river water, but only fractionally, for the area of a river is nothing compared with the area of the country drained by it. The influence of an excessive rainfall on the water of a river is therefore for all practical purposes dependent on the rain that has fallen on the drainage area.

First, then, it is perfectly certain that as a rule, during the first few days of a flood (and for purposes of distinction I will call this *primary flood water*), the water in the river is materially affected for the worse. And the reason is manifest: during the period immediately preceding a heavy flood, when the rainfall is more or less insignificant, matters accumulate in the soil, which if soluble will be dissolved by, and if insoluble will be mechanically suspended in, the rain water as it

passes over the drainage area. Further, the admixture of the fresh rain water with the rain water which has fallen in small quantity during a preceding period, but which has not hitherto found its way into the river, having been for the most part retained by the soil, serves to render the primary flood water heavy in total solid matter, excessive in dissolved organic matter, and more or less turbid. Further, the river at its ordinary rate and with its ordinary power of flow, is wanting in force to carry down a quantity of material, organic and mineral, which accumulates day by day in the higher reaches, the longer the intervals of flood the greater being the accumulation. These, however, are dislodged by the increased velocity of a river at the time of flood. It will easily be conceived therefore how difficult it is to obtain definite facts to show with precision the influence of flood water.

I shall now state certain analytical results which indicate the ill effects of primary flood water in the case of the River Thames.

In the Thames two of the heaviest floods of which I have any personal knowledge occurred in November, 1875, the river being at its maximum on the 18th of the month when the water was about 6 feet 8 inches above summer level, and the other in January, 1877, which reached its maximum about January 11th, the river being on that day 8 feet 2 inches above summer level. The month's rainfall in the latter case was 4·72 inches. I have analyses of the river water taken on both these days. I regret that I have no analyses of the water taken on immediately preceding days in either case, but I have an analysis of the river water taken on November 8th, 1875, that is 10 days preceding the heavy flood, when the river was 2 feet 10 inches

TABLE IX.—*River Thames.*

	Level of water.	Total solid matter per gallon.	Oxygen required by organic matter during 3 hours.	Initial hardness.	Grains of suspended matter per gallon.
1875.		grains.	grain.	degrees.	
November 8	2 ft. 10 in. above summer level	19·24	0·064	14·3	Clear.
November 18	6 ft. 8 in. above summer level	21·27	0·173	16·5	1·18
1877.					
January 2 ..	2 ft. above summer level	17·50	0·038	13·8	Slightly turbid
January 11..	8 ft. 2 in. above summer level	20·10	0·181	14·7	1·26

above summer level, and in the case of the 1877 flood I am able to give an analysis of the Thames water on the 2nd January (that is, nine days before the maximum flood) when the river was 2 feet above summer level. The results are stated in Table IX.

There is, I admit, not quite the increase in the total solid matter in these two cases of flood water that I should have expected, but it must be remarked that both the samples with which they are compared are also samples of flood water, although in a very minor degree. Thus in January, 1877, the flood water had only 20·1 grains of solid matter in solution. The rise in organic matter, however, is well marked in both cases; in the 1875 sample the high flood water requiring 0·173 grain of oxygen per gallon to oxidise the organic matter against 0·064 grain required by the water 10 days previously, whilst the 1877 sample of high flood water required 0·181 grain of oxygen against 0·038 grain required by the sample taken from the river nine days before. It is clear therefore that this primary flood water seriously affects the main river water.

Leaving these two unusual illustrations of flood, I have given in Table X the average analyses of 16 samples of flood water, the river being swollen (with one exception) from 3 to 5 feet above summer level, and for purposes of comparison I have added the average of 20 analyses of Thames water when the river was at or within 10 inches of mean summer level. From these detailed results it will be noted that the solid matter of flood water is 22·84 grains per gallon against 18·61 when there was no flood (that is, an increase of 4·23 grains per gallon), the oxygen required to oxidise the organic matter being 0·194 grain of oxygen in flood water against 0·049 (practically four times as much), whilst the hardness of flood water was 2·8° in excess of the hardness of the water at mean summer level:—

TABLE X.—*River Thames.*

	Total solid matter.	Oxygen required to oxidise the organic matter.	Initial hardness.	Matter in suspension.
	grains.	grain.	degrees.	
Average of 20 analyses when the river was at summer level, or within 10 inches of summer level.....	18·61	0·049	14·0	
Average of 16 analyses when the river was in from 3 feet to 5 feet of flood (primary flood water)	22·84	0·194	16·8	0·8 gr. per gall.

I would merely remark here that the suspended matter in flood water in the Thames varies from a minute trace to about 1·5 grains per gallon.

All the facts then prove that primary flood water is inferior to the normal river water as regards organic purity and general clearness.

The transition from primary to secondary flood water is perfectly definite in practice, although (owing to a variety of circumstances) it is impossible to fix any time when the change will occur. By *secondary flood water* I wish to imply the water that comes down after the river has been in flood for some time. Chemically a great difference may be noted in the water with the altered conditions. The drainage area has been washed clean. All the materials capable of displacement have been displaced, and the water that flows from the country drained by the river, passes slowly from a state of maximum impurity to a state of maximum purity, which continues, and indeed is specially remarkable, during the period of fall from flood to the normal. This change is illustrated by the results stated in Table XI, where I have placed in juxtaposition with the 16 analyses of primary flood water the average result of 10 analyses of secondary flood water, some taken after a considerable period of flood, and others during the period of fall when the river was assuming its ordinary level:—

TABLE XI —*River Thames.*

	Total solid matter.	Oxygen required to oxidise the organic matter.	Initial hardness.	Suspended matter.
	grains.	grain.	degrees.	
Average of 16 analyses of primary flood water, the river being 3 feet to 5 feet above summer level.....	22·84	0·194	16·8	0·8 gr. per gall.
Average of 10 analyses of secondary flood water.....	17·28	0·031	13·4	{ Very slightly turbid

Thus the total solid matter of secondary flood water is only 17·28 grains per gallon against 22·84 grains in primary flood water, the oxygen required being about one-sixth, and the hardness reduced 3°, whilst the matters in suspension are no longer capable of estimation.

I will only add a few words on the condition of river water when the river is at or below mean summer level, which, in the case of the River Thames, is reckoned at 6 feet. On five different occasions I have examined the water when it has been at different levels, from 4 inches below summer level to summer level, with the average result

stated in Table XII. And from these examinations one thing is certain, that the water at such times is not so good as it is in the period succeeding a flood and during a fall, although in respect of appearance merely, the water is undoubtedly brighter and clearer than at any other time. Thus the average of the five analyses give 18·5 grains per gallon of dissolved solid matter, the oxygen used during three hours being 0·067 grain per gallon.

TABLE XII.—*River Thames.*

	Total solid matter.	Oxygen required to oxidise organic matter.	Hardness.	Appearance.
	grains.	grain.	degrees.	
Average of five analyses of Thames water taken when the river was at summer level, to 4 inches below summer level.....	18·50	0·067	14·3	clear.

I have thus far limited my illustrations to the Thames, and I would add here that all the samples, the analyses of which I have quoted in these tables, were taken with the special object of determining the influence of flood water on the river, and they are not (except accidentally, where one sample answered for both purposes) included in the general table (Table III) of unfiltered Thames water, the water examined for this purpose being collected independently of flood or no flood, in the middle of each month.

I could easily multiply observations to show that what I have said about the influence of flood water in the River Thames applies more or less to other rivers.

I shall content myself here with merely a word on that most perfect of flood rivers, the Nile, the analyses of which I have already stated. There are necessarily imperfections and gaps in examinations that are only conducted monthly (the water being taken on a given day), that impair the results as a means of testing actual quality under various specific conditions, although in the Nile these imperfections are less than in any other case. I mention this because I have only one analysis of Nile water during the rise of the river, and this I admit does not harmonise with what I consider the rule of floods. I have arranged in Table XIII the detailed results already given in Table V, under the four heads of low water, water during rise, high water, water during fall, in order to show that on the grand scale pre-

sented to us in this river we have (except in one particular, as I have said, and in this case we have only a single analysis) the same order and general laws that we find in the puny floods of the Thames.

TABLE XIII.—*River Nile.*

	Total solid matter.	Oxygen required to oxidise the organic matter.	Chlorine.	Hardness.
	grains.	grain.	grains.	degrees.
Low water (April, May, June)	13·76	0·230	1·088	7·4
Water during rise (July)	11·47	0·092	0·714	5·6
High water (August, September, October) }	12·11	0·161	0·365	5·6
Water during fall (November to March) }	10·57	0·168	0·371	6·6

But the character of flood water is itself influenced by such numerous circumstances, that it would seem to be impossible to fix any absolute laws. I can only briefly indicate a few of the most important influencing circumstances.

(*a.*) *The Geological Nature of the Drainage Area.*

Not only do the drainage areas of different rivers differ geologically, but the drainage area of the same river may exhibit a totally different character in one part to that which it does in another. Very different for instance chemically is the flood water derived from a drainage area of limestone from one of clay, and both differ from the flood water from an area made up of metamorphic or igneous rocks, such as the slates and quartzites of the Welsh mountains, or the granitic rocks in Cornwall, all of which have been exposed for a long time to severe weather action. Nor indeed is the extent of weathering, to which the same rocks at certain places have been subjected, altogether unimportant.

(*β.*) *The Time of Year at which the Floods occur.*

Here three influencing conditions are manifest, viz :—(1) condition of ground dependent on weather; (2) temperature, and (3) atmospheric influences. The time of year is a circumstance that materially affects the influence of a flood on a river for good or otherwise. Given, for instance, on the one hand rain falling on a dry ground, in hot summer weather, when evaporation is at its maximum, and oxidation has been unusually active, so that the putrescent organic matter of the drainage

area is reduced to a minimum, and given on the other hand rain falling on ground saturated to the full, in cold winter weather, it is manifest that very different results must accrue. In one case much of the water that falls is retained by the soil, whilst that which finds its way into the river is barely, if at all contaminated, while in the other case, the rain falls on ground that can hold no more than it has. A quantity of water equal to the total rainfall must, under these latter conditions, find its way into the river; a quantity, I say, equal to the rain that has fallen, but not necessarily the rain itself that has just fallen, for by the force of its fall it displaces some part, and gets mixed with much of the remainder of the water that has for a long period soaked and remained in the ground, and which by long contact with organic impurities, adds materially to the impurity of the river. And analysis shows that this is so; in other words, that a summer flood produces a very different effect on the river water to a winter flood. I may give in illustration of this fact the analysis of the water of two floods of nearly the same extent in the River Severn, the first taken in July, and the second in December of the same year. In July the water on the second day of flood was practically no worse than the water immediately preceding the flood, the oxygen required in the two cases being the same to the second decimal place, whilst the total solid matter of the flood water was slightly less than was found in the specimen examined immediately before the flood. In the December flood (and I may add that the samples to which I am alluding were collected at the same spot in the river) the oxygen required by the flood water on the second day was 0.161 grain against 0.030 grain required by the water immediately preceding the flood, the total solid matter being increased by nearly 5 grains as the result of the excessive rain.

(γ.) *The Interval that has elapsed between one Flood and another.*

I believe the following fairly expresses the influence of interval on a flood. If it be *summer*, the longer the interval (so far as organic purity is concerned) the better the water, but if it be *winter*, the longer the interval the worse the water.

(δ.) *The exact Time occupied by a given Rainfall.*

My experiments show that if 0.5 inch of rain falls in one hour on a drainage-area, it would render the river water for a time far more impure than if the 0.5 inch fell in 3 hours or in the 24 hours, because the greater force of the rain in the case where the fall only occupied one hour, would affect a more complete and absolute dislodgment of the accumulated impurities than would be occasioned by the lesser force, where the same quantity of rain fell slowly.

I draw one general conclusion from this part of my subject. If river water be used as a supply, a river subject to frequent floods is not necessarily a disadvantage. In advising what water should be taken into the reservoir, and what rejected, in order to avoid the bad and not lose the good, and remembering the general law that the last day of low water is worse than the first, and the first day of high water worse than the last, the chemist can immensely assist the engineer by an accurate study, at the spot where the works are to be constructed, of the average period of primary flood water. This undoubtedly should as far as possible be avoided for distribution, provision being commonly made for the purpose by the construction of storage reservoirs.

(2.) *Peat, or Vegetable Impurity.*

Authorities distinguish several kinds of peat, according to differences in colour and age. Thus in some cases peat is white, and from this we meet with various gradations of colour and degrees of chemical change, until we reach samples absolutely as black as coal. As regards the so-called white peat, it is not, as has been suggested, bleached peat, but simply new peat formed by the dying away of the last crop of the special plant or plants from which it is formed, and which dead material itself constitutes the bed upon which the new crop grows.

But for water chemists these distinctions are of little importance. Practically the classification into (1) *old* peat, and (2) *recent* peat, is enough for all purposes. The best means (if indeed it be not the only laboratory means) of determining which of these two forms be present in a water, is the two-foot tube—in other words the colour presented by a water when viewed through a stratum of considerable thickness. The *yellowish-green tint* sometimes observed indicates very recent peaty matter; the *brownish olive-green tint* is characteristic of less recent, but yet of comparatively fresh peat; whilst the *true brown coffee tint*, free from a shade of olive-green, is more or less distinctive of old peat. On this point I fear little more that is definite can be said.

Of course we do not often meet with these well marked divisions, the old and the new being as a rule intermixed; but still in many cases with practice the tint of a water is sufficient to establish not only the *presence* of peat and the *quantity* of peat, but even the *kind* of

In considering this question, I have again to plead for the valuable indications afforded by the two-foot tube, in opposition, I regret to say, to the expressed opinion of certain authorities. In this I shall be excused for my affection, for it is only natural, because whilst I am

unable to claim the position of parent, I was present and even in a small degree assisted at its birth.

Of course, the two-foot tube will not take the place of analysis, but it will assist analysis. Mixed with vegetable matter there may be animal matter, the tint of the peat (that is the harmless organic matter) overpowering the tint of the animal contamination. But the story told by the two-foot tube in its bearing on the analytical data is most important. Thus 0.4 part per 100,000 of organic carbon or 0.2 grain of oxygen per gallon would have a very different significance to the chemist if the tint exhibited by a large bulk of the water under examination was of a definitely brown coffee colour, indicating vegetable matter, to what it would if the water was colourless or of a yellow tint.

Again, as I have said elsewhere, the quantity of peat may be fairly inferred from the tint-depth.

Supposing you have an undoubtedly peaty water containing an evident admixture of both old and recent peat, but (from the history) free from animal contamination, the following general conclusions, the results of numerous experiments on the quantitative indications of the two-foot tube, may I believe be regarded as fairly accurate:—

If the water in the two-foot tube exhibits a *greenish tint*, or a colour short of an olive-green tint, but exhibits no colour in a quart decanter, the quantity of peat in the water is less than 0.1 grain per gallon.

If the water in the two-foot tube exhibits an *olive-green tint*, passing into an olive-yellow but *short of a brown tint*, exhibiting no colour when placed in a quart decanter, the quantity of peat in the water may be regarded as varying from 0.1 grain to 0.2 grain per gallon, according to the tint-depth recorded.

If the water in the two-foot tube exhibits a more or less marked *brown tint*, that is from a brown shade to a well-defined brown discoloration, the water at the same time exhibiting a distinctly peaty tint in a quart decanter, the quantity of peat in the water may be regarded as varying from 0.2 to 0.5 grain per gallon according to the tint-depth.

If the water contains one grain of peat per gallon, the two-foot tube shows it of a *porter tint*.

If the water contains 2 grains of peat per gallon the two-foot tube shows it as *black*.

I do not wish to be misunderstood in stating these general conclusions. The two-foot tube is in the laboratory a mere adjunct to analysis—a not unimportant adjunct it is true. It is impossible, however, to overrate its value in the inspection of a district for the purpose of advising in matters of water supply, and from practical experience I strongly recommend it as a travelling companion. A Hofman's furnace, a Sprengel pump, and a Frankland's eudiometric apparatus are

inconvenient luggage. A two-foot tube will not of course reveal what these reveal when properly used, but I am convinced that its revelations are singularly valuable and far from inaccurate.

And here I would remark on two difficulties that have been suggested in connection with its use:—

1. The fact that the tints of different kinds of peat vary to a very marked extent. This as I have said is true, but I may add that a tint depth of one colour may always be compared roughly with the tint depth of another colour, and that for practical purposes variations in tint are of little importance.

2. The second difficulty was first suggested to me by Dr. Frankland, and deserves consideration, viz., that the peat in a water may by oxidation be bleached, the water thereby being rendered colourless, without the actual quantity of peaty matter in the water being lessened. Theoretically I admit this to be true—practically I question if it ever occurs. At any rate I have never known a case, except as a laboratory experiment, where I could persuade myself that the water of a river was simply colourless because the peat in it had been bleached.

And this leads me to speak on the removal by oxidation or otherwise of peat in running water, in other words, the natural means whereby purity from excessive vegetable matter in a river is maintained.

I have had opportunities, during a fortnight's inspection professionally, of studying this subject in that most wonderful of peat rivers, the Shannon, along a run of very nearly 50 miles (from Portumna to Limerick), the river receiving throughout the whole course examined, not only feeders containing, except in one or two cases, an even larger quantity of peat than itself, but the drainage, of a deep coffee tint, and in not inconsiderable streams, from huge bogs covering many square miles of country.

I am aware that I am now entering upon a subject where great differences of opinion exist, and I would approach it cautiously. (See Table.) Let me then put the case of the Shannon leaving Portumna containing a quantity of peat represented by 0.9 of organic carbon per 100,000 (for in arguing this question of oxidation I shall in the main appeal for manifest reasons to the indications of the combustion process), receiving as it continues to flow an enormous quantity of black peaty matter, and streams much more peaty than itself, and drainage from an area that can only be described truly as a peat bog. Should we not expect, I ask, if the water contained in itself no inherent power of purification (I mean of course the power of effecting oxidation of the peat), that a sample examined 35 miles further down the river, say at Castle Connell, would contain an enormously increased quantity of peaty matter? But the reverse of this is the case. For no

only does the two-foot tube tell that the peat is manifestly less, but on analysis the organic carbon at Castle Connell is found to be only a little over one-half what it was at Portumna. What then has become of it? Certain it is the peat could not have evaporated, and I confess I can invent no possible explanation of its disappearance except by believing that in the course of its flow it has been oxidised by the oxygen held in solution by the water. At any rate those who hold non-oxidation in running water must explain how it is that the absolute organic carbon by a flow of 35 miles (even in the face of the fact that the river in the course of its flow is receiving enormous volumes of highly peat-charged water) is lessened in so remarkable a degree.

But from this long river run I proceed to flows of far shorter distance, in order to state more definitely the conditions influencing oxidation.

Lough Derg is a lake 25 miles long, formed by an expanse of the River Shannon. A large quantity of peaty land drains into it. Hence, the difference in the quantity of organic carbon found in the water collected at the south of the lake over that found in the water collected at the north, in no way expresses the actual quantity of peat oxidised during the passage of the water through the lake. Nevertheless the organic carbon at the southern junction of the lake with the river is less by 0.180 per 100,000 parts to that found at the northern junction. A third sample was taken one mile below Killaloe. As a matter of fact there is less bog drainage going into the river in this short run than at any other spot in the 50 mile flow examined, although even here the quantity finding its way into the river is not inconsiderable. Nevertheless in the course of this one mile flow the organic carbon fell from 0.800 to 0.48. Incidentally I may mention that these results were confirmed by the oxygen process, and by the appearance of the water in the two-foot tube. From this point to within half-a-mile of Castle Connell, the quantity of peat drainage that enters the river is enormous, indeed an extensive peat bog covering miles of country pours into the river its absolutely black drainage water in full-sized streams. At O'Briens-bridge, the organic carbon was found again to have risen to 0.840 per 100,000, and I have no doubt from the two-foot tube observations, although I have no analysis in proof, that below this spot the quantity of organic carbon would have been even greater. This highly peaty water, after a *very short run indeed*, although (and I must again insist on this point) here and there receiving notable quantities of bog drainage, becomes very manifestly less peaty, the organic carbon being reduced from 0.840 to 0.593 per 100,000 parts. How can this remarkable result be accounted for? Thus. Between the two points where these samples were taken, are to be found the far-famed falls

of Castle Connell, where in the course of a few hundred yards the level of the river sinks nearly 50 feet. The extent of aëration the water must undergo in these magnificent falls must be considerable. The part they play in effecting the purification of the water was strikingly manifest in comparing the dark tint of the water as it foamed and bubbled over the rocks with which it first came into contact in the upper part of the Doonas falls, with the comparatively light peat tint the water exhibited as it played over the rocks situated at the lower parts of the falls. I watched these changes of tint for some hours along the course of the falls, and a more magnificent natural experiment I never witnessed. If this alteration in actual quantity as shown by analysis is not oxidation, I am totally at a loss to conceive what it can be.

Leaving the Shannon for a moment (for I shall have occasion to refer to this river again), I am desirous of giving a different kind of illustration, and a most striking illustration too, in proof of the oxidation of peat in running water freely exposed to the air. At a certain water company's works in the north of England where the water supply is of a peaty character, a large supply reservoir near the town is filled from a storage reservoir, situated at a distance of 6,820 yards from the supply reservoir. The water is delivered into the supply reservoir by two channels, the one being a closed iron pipe, and the other an open brick conduit. The fall between the two reservoirs is about 401 feet. Both channels leave the supply reservoir by the same pipe, the pipe dividing soon after leaving the reservoir. My attention was called to the extraordinary difference in the tint-depth of the water from these two channels when it reached the supply reservoir, and the manager at the works assured me it would be manifest even if samples were placed side by side in decanters. And so it proved. The water that flowed through the open channel was nearly colourless, whilst the water taken from the closed pipe exhibited a well marked peaty tint. I took samples of both waters, and afterwards collected a sample from the supply reservoir. The sample from the reservoir gave 0.461 of organic carbon per 100,000. The sample from the closed pipe gave 0.49 (*i.e.*, practically the same as in the reservoir sample), whilst the organic carbon in the water from the open pipe was 0.23 part per 100,000. This to my mind is a perfect experimental proof of the oxidation of peat.

One more word only on this. The oxidation of *vegetable* matters is (as I shall show directly) infinitely less rapid than the oxidation of *animal* matters. More easily affected it is true by oxidising reagents, peat resists more effectually than animal matters (nevertheless it yields in time) the action of free oxygen.

At this point, having proved I think satisfactorily the oxidation of

peat in running water, I am desirous once again of referring to a distinction (which it is advisable should not be forgotten) between the mere *bleaching* of peat and its *oxidation* (by which I mean its entire destruction or burning up). I am ready to admit the possibility of the two-foot tube exhibiting a colourless water in which the proportion of bleached peat might be considerable.

An experiment, not conducted however for the special purpose, has to my mind conclusively proved the possibility of bleaching peat. In about a quarter of a gallon of very peaty water rendered acid with sulphuric acid (it was in fact the Shannon water taken at Portumna, and giving 0.980 of organic carbon per 100,000 parts of water) I inserted two platinum plates (6 inches by 3 inches each), and connected them with four pint cells of a Grove's battery. The connection had not been made more than a few seconds, when, on giving the vessel containing the water a slight shake, I noticed that the water became perfectly colourless, a change manifest as the vessel was standing at the time on a white card. I certainly did not expect this, and instantly disconnected the poles. An analysis was then made of the water. The organic carbon of this colourless water was 0.874 against the 0.980 of the original water. The results were so nearly alike that it was evident very little of the peat had undergone oxidation during the process. I then took another portion of the same water and submitted it to electrolysis, when precisely the same change occurred within a few seconds. In this experiment, however, I allowed the electrolytic action to proceed for a very considerable time, and again made an analysis of the water, when I found the organic carbon was only 0.084 part per 100,000. It is evident that in the first experiment, bleaching as a precursor to oxidation had been effected, and I have no doubt that I might have arranged the experiment as to stop the electrolytic action at such a moment, that even a smaller quantity still of the peat would have been oxidised. I think it right to mention that since making this experiment I have tried several other peaty waters in a similar manner, but for some reason or other (as yet beyond my comprehension) I have failed to obtain the well marked results that I observed in the case of the Shannon water, although in all cases the results were fairly well marked. I propose before long investigating this matter more carefully, and at present I merely place the fact on record. Theoretically then I am prepared to admit that the bleaching of peat precedes its complete oxidation, so that a colourless water may still contain a considerable quantity of dissolved peat. Practically, however, I think the distinction between bleaching and oxidation is of no importance. If all the peat that found its way into the river entered at one spot only in its flow, it is not unlikely that the water would lose its colour before the peat (*quâ* peat) disappeared—that is

—was oxidised. Under such practically impossible circumstances, the distinction might (I do not say *would*, for peaty matter is as harmless as a potato skin) be important.

There is one other way in which I am convinced the quantity of peat in a river may be, and often is, considerably reduced—that is by the admixture of some feeder, containing a large quantity of solid mineral matter in suspension, with the peaty river.

Let me once again in illustration of what I mean refer to the River Shannon.

The Limerick Water Company derive their supply from the Shannon. The intake is situated at a spot about two miles lower down the river than where the River Mulcaire enters. The River Mulcaire contains considerably less peaty matter than the main river, and so far as animal contamination is concerned would satisfy even the Rivers Pollution Commissioners. But the Mulcaire is a singularly thick and turbid stream, the turbidity being due to red sandstone drift mixed with more or less road mud. The question submitted to me was whether it would not be advisable to remove the intake of the Company above the Mulcaire, in order to avoid the turbid water brought down by this river. At first, having a well-known case connected with the Thames in my mind, and perhaps unwisely inclined to yield to the popular notion that turbidity means impurity, I was disposed to recommend the adoption of this course. But on investigating the subject closely, I was driven to the conclusion that the admixture of the turbid Mulcaire with the main river was an absolute, and by no means an insignificant, advantage to the Shannon water. Thus just above the junction of the Mulcaire the organic carbon in the river was found to be 0.914 part per 100,000, the oxygen required being 0.373 grain per gallon. For here in passing let me remark that no sooner had the magnificent falls of Castle Connell done their work in reducing the peat by the efficient aëration they effected, than floods of peaty drainage again find their way into the water, and so bring up the amount of peat in the river to a quantity almost equal to that found at Portumna. But again a natural process of purification, and this time of a different kind, occurs. The thick Mulcaire joins the river, and the admixture of the apparently impure water, is the means of effecting purity. The mineral matter it would seem as it subsides carries down with it the peat, held as we say in solution, but which probably in the case of peat merely implies mechanical suspension, the individual particles being so finely divided that our vision fails to detect them as individual particles. A quarter of a mile from the junction of the Mulcaire the organic carbon has fallen from 0.914 to 0.61 part per 100,000, and the oxygen required from 0.37 to 0.27 grain per gallon.

I further attempted to decide this question by a laboratory experiment. The clear water of the Mulcaire (that is, a sample where the matters in suspension had been allowed to subside) gave 0.212 of organic carbon per 100,000. A sample of peaty Shannon water that gave 0.800 part of organic carbon per 100,000 (in fact the water collected at Killaloe) was well shaken with an equal volume of the Mulcaire water that had been previously examined (giving organic carbon 0.212), save that in this case the matters in suspension were not removed. The suspended matter in the mixed sample was then allowed to subside, and the clear water syphoned off. This on analysis gave (not 0.506 part of organic carbon per 100,000, which would have been the mean analysis of the two waters, but) 0.214 part of organic carbon per 100,000, a result which proved beyond question that the admixture of a turbid feeder may be an advantage to a river, and serve as a means of purification. My advice accordingly was not to alter the position of the intake.

These, then, in the case of peat are the natural means whereby the quantity in running water is kept in check:—

1. *The inherent power that water possesses of self-purification from the oxidation of the peat by the oxygen held in solution in the water.*

This process is enormously helped by certain natural and physical conditions, whereby the more complete aëration of the water and the more intimate contact between oxygen and peat is effected.

2. *Mechanical precipitation by admixture with coarse mineral suspended matter.*

The artificial means of purifying peaty water are storage, subsidence, and filtration. These I leave for the moment.

(3.) *Sewage or Animal Pollution.*

From peat I pass to animal impurity; in other words, to the pollution of river water by sewage. From the consideration of the harmless we are thus led to the consideration of what may be harmful. I agree with Dr. Frankland in regarding this as, to use his own words, “a subject of vital importance.” I admit no distinction, however, between healthy and unhealthy sewage, but regard it all (as I contend it should be regarded) as unhealthy and absolutely objectionable in water used for drinking. Hence in discussing the removal of sewage in running water our grounds of argument must be surer than in the case of peat, and our experiments more searching.

The two questions we have to discuss are:—

First. Does the water of a river having been once polluted by admixture with sewage, again, after a moderate flow, assume its original state of purity? In other words, does running water possess any power of self-purification.

Secondly. If such natural process there be, what are the conditions requisite for its fulfilment, and what are the circumstances affecting those conditions.

Let me briefly state my case, and then proceed to call my evidence:—

1. If sewage be discharged into running water, the organic impurities will, I contend, after a flow of a few miles, be entirely destroyed or got rid of, the water once again assuming its normal condition of purity.

2. That this power of self-purification depends upon three things—

(*α.*) On the *subsidence* of the suspended impurities brought down by the sewage. Thus, in the course of the river flow, the grosser suspended matters will be left behind.

(*β.*) On the presence of *animal life* in the river. After the water has assumed a certain degree of purity (for it is not till then that animal life thrives), the fish in the river act as river scavengers, and so as general purifying agents.

(*γ.*) On the *oxidation of the organic matter*. The dissolved oxygen is derived partly (and in the first instance entirely) from the air, and partly (more especially in the later stages, when the water has reached a certain purity, and vegetation begins to reappear) to plant life, vegetation constituting an important means whereby oxygen is set free in the water itself. Such oxygen is probably in a more than ordinarily active condition to effect the oxidation of the organic impurity.

3. That the rapidity of the oxidation of the organic impurity depends amongst others on the following conditions—

(*α.*) On the degree of dilution of the sewage with pure water.

(*β.*) On the distance of run.

(*γ.*) On the rapidity of the current.

(*δ.*) On the temperature.

(*ε.*) On certain natural or artificial physical conditions, such as the nature of the river bed (that is, whether it be rocky or otherwise), the occurrence in the course of the flow of falls, weirs, locks, &c., whereby the breaking up of the water particles, more efficient aëration, and the necessarily more complete actual contact of the organic matter with the oxygen necessary for its combustion, are effected.

I will not trouble the Society with any details either on the curious influence of subsidence, accompanied as it is by a sorting of the suspended matters, or on the influence of fish as river scavengers, but confine myself entirely to the vexed question of oxidation in running water.

Without attaching any undue importance to the argument by analogy I might fairly ask, is not this burning up or oxidation of the organic matter in running water exactly what we should anticipate

would happen? Is not the air itself daily receiving vast masses of organic *débris*, myriads of dead epithelial scales from every membrane visible and invisible, from the skin sound and healthy, and who doubts for a moment but that the air acts on this sewage matter both mechanically, thereby dividing the noxious particles, and chemically, thereby burning them up, and preventing them from acting injuriously? Are men never to drink water because it has been once contaminated and rendered impure by sewage? As well tell me that men must never breathe an air that has once been polluted by the scales of a person suffering from scarlet fever, or the infected breath of a measly patient. If oxidation purifies in the one case, may not oxidation be expected *à fortiori* to act in the other, "dissolved oxygen," to quote Dr. Frankland's words, "being well known to be chemically much more active than the gaseous oxygen of the air."

In proof of the oxidation of sewage in running water I desire to direct attention to three kinds of evidence:—

A. *The naked eye inspection of rivers receiving sewage.*

If we examine a river at and a little beyond the spot of a sewage discharge, it will be observed that the admixture of the sewage with the water of the river is at first more or less imperfect, the line of the sewage stream being distinctly marked for some distance. Gradually we shall note the sewage path widening, the edges becoming less and less defined, until after a certain run, the exact distance being dependent on many circumstances unnecessary to specify now, the mixture of river water and sewage will be complete.

But there is more than this to be noted. The sewage at the out-fall is probably offensive, very turbid, and more or less brown, the exact colour and degree of offensiveness being dependent partly on the character of the sewage, but chiefly on the distance it has travelled along the mains before its discharge into the river, and the extent of exposure it has undergone. Tracing the sewage stream down the river it will be seen to assume a black colour from the formation of sulphide of iron. A further short distance and the black colour perceptibly decreases, and as we watch the flow, the blackness, I had almost written yard by yard, disappears, until at last the river water exhibits no signs of colour, turbidity, or smell.

Once again, very soon after sewage has been turned into a river, the sewage fungus, that most absolute indication of the presence of sewage in any quantity, makes its appearance in the river. Excepting this, however, all signs of vegetable life, barring possibly a few straggling weeds, disappear; no fish, or fish only of a certain kind, are to be seen. The banks and river bed become black, and branches of any trees that by chance dip into the water will be seen covered with a

black flocculent deposit. A short distance further down the river (and sometimes a very short distance indeed) the sewage fungus cannot be found, vegetation becomes clean and luxuriant, fish are abundant, and the river banks and the river bed seen through the now clear water show no signs whatsoever of that black deposit observed higher up the river.

These are no fancy sketches. I will merely give one or two illustrations. I have seen the River Soar at Leicester black with sewage, no river vegetation being visible. I have seen it the day following at Loughborough (a distance of 13 miles down river from Leicester) perfectly clear, the river banks clean, and fish abundant.

I have seen the River Irwell at Manchester polluted with every form of filth, personal and manufacturing. At Warrington, after a flow of nine miles, the offensive character of the stream had entirely disappeared.

The River Skerne receives the sewage of Darlington. It is a filthy stream, loaded with the sewage fungus, and without fish or vegetation. Three miles from where it receives the Darlington sewage, it joins the River Tees. Even in this flow the practically undiluted sewage has manifestly improved. I have watched thousands of not delicate fish at the very entrance of the Skerne feeding in their scavenging capacities on the organic impurities brought down by it. But even they contented themselves with remaining in the Tees at the point of junction. One mile from the junction of the Skerne, the River Tees is beautifully clear, the banks clean, vegetation healthy, and fish of all kinds abundant. And the mere naked eye inspection records an absence of that horrid pollution that the Skerne brings into the main river.

One other illustration only I will give,—a very small case it is true, but one where circumstances allowed me to trace changes by flow, independent of any possible after-admixture of pure water to dilute, or of further mixture with sewage to pollute, in a more definitely satisfactory manner than is common.

The sewage of Killaloe (a village of about 500 inhabitants, but without any drainage system) flows into a canal of very moderate size, which runs side by side for about two miles with the River Shannon. For about 200 yards after it receives the Killaloe drainage, the canal water is black and turbid, the banks dirty, and there is an absolute absence of vegetation. About 300 yards from the out-fall there is a lock, and, the trade of the canal being brisk, a continual opening and shutting of the lock gates is rendered necessary, constant motion being thereby imparted to the canal water. The condition of the canal banks and the water on the far side of the lock is remarkable. At a very short distance from the lock gates, there is

a clear bright water, comparatively clean banks, and most luxuriant vegetation, comparing in a striking manner with the polluted state of the water and the dirty banks on the side of the lock into which the sewage is being discharged.

I could multiply instances indefinitely of a like kind. This much seems certain—given black banks, turbid dirty water, the presence of the sewage fungus, the absence of fish and vegetation, *the presence of sewage* may be inferred. Given, on the other hand, clean banks and a clean river bed, clear water, the absence of the sewage fungus, luxuriant vegetation, abundance of fish, and the presence more especially of such delicate molluscs as the fresh water limpet, *the absence of sewage* is indicated.

If these conditions, indicating at one spot the presence of sewage and at another spot the absence of sewage, can be distinctly recognised at different spots in a river, it may surely be taken for granted that the river possesses a power of self-purification whereby these changes are effected.

B. From this appeal to the naked eye inspection of rivers let me pass to certain analytical results.

There is first of all a remarkable fact to be noted in the analyses of Thames water. The water at Lechlade may be regarded as having assumed as nearly as possible the character of river water. Up to this point it will be conceded that practically no sewage has found its way into the river. Between Lechlade and Hampton, a distance of 110 miles, the river received (I am speaking of a few years ago) the sewage of nearly a million people. At certain places it is admitted that a larger quantity of organic matter than was present at Lechlade could be detected in the water. For instance, one mile below Reading I have found a quantity of organic matter at least double that indicated at Lechlade. But four miles further on, the water was again found to have become normal, whilst the organic carbon and nitrogen at Hampton, notwithstanding the sewage of this million of people, was rather less than at Lechlade. What I ask had become of the sewage of this million people, if it had not been oxidised during the flow of the river?

Again take the Severn. The sewage of Worcester (population 34,000) is discharged into the river. For a short distance beyond the outfall, the analysis shows a very marked increase in the organic impurity of the river water. But this increase rapidly decreases. The organic carbon (see Table VII) one mile below the sewer outfall, is 0.510 part per 100,000 against 0.842 near the mouth of the outfall. At two and a quarter miles below Worcester (the River Teme having meanwhile joined the main river), the Severn water was found to

contain only 0.101 of organic carbon. The oxygen process told identically the same story. Thus 0.164 grain of oxygen was required by the water near the sewer outfall, and only 0.040 grain per gallon at a distance of $2\frac{1}{4}$ miles. It is true the organic matter again rises as indicated both by the oxygen and combustion processes, but it would answer my purpose equally well, in proof of oxidation, to take the river water at any spot up to Tewkesbury to show an absolute lessening of the organic matter in the course of the river flow. I should wish to add that all the samples examined were taken on the same day, and that Professor Ansted (who accompanied me) and myself, both saw the sewage at Worcester on the day in question flowing into the river. Further, similar results were obtained by Dr. Odling and Mr. Crookes, whom I accompanied on a second inspection, journeying on this occasion up the river in a steamer from Tewkesbury to Worcester, collecting samples *en route*.

Again, let me refer to the River Wear. From Bishop Auckland to Durham the river receives (inclusive of that from Bishop Auckland) the sewage of about 100,000 people. Above Bishop Auckland the unpolluted river was found to contain 0.187 of organic carbon and 0.032 of organic nitrogen per 100,000 parts, the oxygen required being 0.050 grain per gallon. Two hundred yards below the Bishop Auckland outfall, the river water was manifestly sewagey, the banks were dirty, the water turbid, and vegetation sparse. The organic carbon had risen to 0.260, and the organic nitrogen to 0.070 part per 100,000, the oxygen required being 0.070 grain per gallon. After a flow of half a mile the blackness of the river disappeared, whilst at Durham, a distance of but 13 miles from Bishop Auckland, the river water showed a far greater degree of purity than even above the sewer outfall at Bishop Auckland. Thus it contained 0.150 organic carbon, 0.028 organic nitrogen per 100,000 parts, and required only 0.040 grain of oxygen per gallon to oxidise the organic matter. The fact is, the River Wear is from its rocky bottom, a series of natural weirs, so that by the intense mechanical action to which the water is subject, not merely is the whole of the sewage of Bishop Auckland (and any other sewage that finds its way into the river) oxidised in the course of the run, but some of the organic matter that was in the river before it reached Bishop Auckland is also oxidised. Similar results indicating the same facts were obtained by Mr. Crookes, with whom I was associated in the investigation. But the Sixth Report of the Rivers Pollution Commissioners is the strongest of all evidence on this matter that I can adduce. So satisfactory is the analysis of the River Wear water at Durham, that notwithstanding it contains the sewage of 100,000 people, and in the face of a gentle protest against a sewage contaminated river as a public supply, they describe it as "*a good water*."

There is one point suggested by the analyses of the water of the River Wear worth recording, and that is, that not only does the organic matter become oxidised, but the water at Durham is absolutely free from nitrates. No doubt they were formed, but at any rate they do not reach Durham. The diminution of the chlorine in a sewage polluted water after a certain run until it assumes the normal of 1 grain or thereabouts per gallon is interesting. Probably the excess of chlorine which is brought into the river by the sewage is taken up by vegetation.

I could multiply instances of this kind, but it is time that I should refer to the evidence adduced by Dr. Frankland, pointing as it does in a diametrically opposite direction, in that most perfect model of painstaking industry, the Sixth Report of the Rivers Pollution Commissioners.

Limiting myself for the moment to river experiments, Dr. Frankland's facts show (at least so he states) that the organic matter is not oxidised appreciably by the flow of a few miles. If I were hypercritical, it would be easy to prove from Dr. Frankland's own analyses that a very manifest disappearance of organic matter does occur, but I let that pass. We thus have Dr. Frankland's facts indicating no oxidation, *versus* my facts indicating oxidation. Far be it from me to question the results of so careful an observer as Dr. Frankland, nor would I for one moment compare the importance of my own work or experience to that of his. Still, I submit that the facts of the actual reduction of organic carbon and nitrogen between two spots in a river are of much greater value than any analyses indicating the reverse, for the reason that Dr. Frankland cannot say that the organic matter found at spot B where he collected his second sample, is the *identical* organic matter that was in the river at spot A, where he took his first sample. And unless he can prove this identity of the organic matter in the two samples, I submit that experiments showing a similar quantity of organic carbon at two spots as proof of non-oxidation, cannot be compared as a matter of evidence with experiments showing a reduction of organic carbon between two spots as proof of oxidation.

Let me explain my meaning by an illustration. Six passengers get into a carriage at a station—call it No. 1. At station No. 3 from the first, there are still six passengers found in the carriage. In the absence of definite evidence to show that the six passengers at No. 3 station are the same six passengers that got into the train at No. 1 station, there is nothing to prove that the whole of the six passengers that got in at No. 1 station did not get out at No. 2 station, and six fresh passengers get in. But if on arriving at No. 3 station, I only find two passengers in the carriage, there being direct evidence there were six in at starting, it is absolutely certain that four at least must have

got out at the intermediate station, whilst the whole six may have got out and two new passengers got in.

Nor has Dr. Frankland overlooked this manifest difficulty. He says, "These (results) must not be interpreted too strictly, since it is evident that the proportions of the different constituents of river water so highly polluted must vary considerably from time to time at any given place in the stream. It is impossible to follow the same body of water for several miles down a stream, because different portions of the stream in the same transverse section move with different velocities, and therefore no body of water included between two transverse sections of a river can retain its identity whilst flowing down the stream." No doubt that is true, but it is a remarkable fact that Dr. Frankland in again referring to this as a source of error merely refers to the *entrance of unpolluted water* into the river, thereby *lowering* the actual percentage of organic carbon and nitrogen, but he takes no notice of what, in my experience, is of far more frequent occurrence, viz., the *entrance of polluted matter*, thereby increasing the organic carbon and nitrogen. (Sixth Report, p. 135.)

At this point Dr. Frankland describes experiments of a different kind. He thoroughly shook together (he states) a mixture of water with 10 per cent. of sewage. He exposed one sample to air and light for 96 hours, and another for 192 hours, and finally syphoned off the mixture three or four times from one bottle to another. On analysis of the water before and after this operation, he found the organic carbon and nitrogen practically identical. Dr. Frankland adds, "These results indicate the effect of oxidation which would be produced by the '*flow of a stream*' containing 10 per cent. of sewage for 96 and 192 miles respectively at the rate of one mile per hour." Here I join issue with Dr. Frankland entirely. The results indicate the amount of oxidation that took place under the conditions of the experiment, but not the amount of oxidation that would take place by the flow of a stream. For similar reasons I demur to the conclusions drawn from the mixture of urine and water treated similarly, in this case simple agitation only being adopted.

I will not pursue these criticisms further. One thing to my mind was certain, that to make any laboratory experiments that would compare in any measure to what goes on in a river, it was absolutely necessary that the water experimented upon should be *running*, and not merely exposed to light and air in a bottle.

C. Experiments on Oxidation.

I will in the first place describe briefly the apparatus I have employed in my experiments on oxidation. It consisted of a series of 20 troughs, each 10 feet long, and constructed of two pieces of

wood joined together at a right angle. Each trough was so placed that it had a fall of one inch, the water from one trough being discharged into a second placed under, but a few inches distant from it. The fall of this second trough was in the opposite direction to the first, the second trough allowing the water to fall in like manner into a third placed under it, the fall of which was in the opposite direction to the second, but in a similar direction to the first, and so on and on, by which means a constant flow of the water to be experimented upon through the 20 troughs was obtained. At the top of the apparatus a cistern was placed, constructed of sufficient size to hold the entire bulk of the water experimented upon. From this cistern, a constant flow of the water through the troughs was maintained. A second cistern of similar size was placed at the bottom of the apparatus, so that all the water from the last trough of the series was delivered into it. The water from the lower cistern was continually pumped by a small force pump into the one above.

I cannot describe the numberless difficulties that we had to encounter in the course of our experiments. At first I am bound to acknowledge all my results showed absolutely against my views of oxidation, but the reasons were manifest. It was not until I had had the whole of the troughs lined with glass and cemented to the wood, so as to avoid the contact of the water and the wood, and had numerous contrivances erected to keep out "the blacks," which were constantly at first interfering (at one time I feared hopelessly) with my organic carbon determinations, that our apparatus worked successfully. I do not propose troubling the Society with my failures, but I may be allowed to say this, that the series of experiments embodied in the following tables were made, one after the other, with unbroken regularity. I hope someone will repeat my experiments, and feel the same gratification that I felt in fighting with, and I flatter myself proving victorious over, an air polluted with dust and soot.

Here allow me to express to Mr. Hart, F.C.S., of Kingsland Green, my thanks for the able and suggestive assistance he rendered me throughout these investigations. In fact, it would have been impossible for me to have continued them, seeing our difficulties, had I not found in him such an excellent assistant.

TABLE XIV.—*Experiment 1 (July 1st).*

Water employed.—Plain New River water drawn direct from mains.

Quantity.—Six gallons.

Distance Travelled and Time occupied in the whole Experiment.—One mile in 8·5 hours from 3 P.M. to 11.30 P.M.

Time.	State of weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Barometer inches.
3.0 P.M.	Cloudy : much wind	67·5°	66·0°	29·85
4.0 "	"	66·5	65·0	"
5.0 "	"	65·0	63·0	"
6.0 "	Slight rain : windy	63·0	60·0	"
8.0 "	"	62·0	59·5	"
11.30 "	"	60·0	57·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per	100,000.	grains.
Before experiment.	0·048	0·114	0·026	1·050
After experiment.	0·037	0·093	0·020	1·050
Results of one mile flow	— 0·011	— 0·021	— 0·006	0

Experiment 2 (July 2nd).

Water employed in Experiment.—New River water containing 5·55 per cent. of sewage (= 1 to 18).

Quantity experimented on.—Six gallons.

Distance of Travel and Time occupied in the whole Experiment.—One mile in 8·5 hours.

Time.	State of weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
11.30 A.M. ...	Wind W. Slight rain	58·0°	58·0°	29·8
12.30 P.M. ...	" Cloudy; no rain	57·5	56·0	"
2.0 " ...	" "	60·0	57·0	"
3.0 " ...	" "	64·0	61·0	"
5.0 " ...	" "	61·0	59·0	"
8.0 " ...	" "	57·0	55·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per	100,000.	grains.
Before experiment	0·391	0·436	0·156	1·40
After experiment	0·181	0·274	0·100	1·44
Results of one mile flow	— 0·210	— 0·162	— 0·056	+ 0·04

Experiment 3 (July 3rd).

Water employed in Experiment.—New River water, containing 6·6 per cent. of sewage (1 part in 15).

Quantity Experimented on.—Six gallons.

Distance of Travel and Time occupied in the Experiment.—One mile in 10·5 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
9.30 A.M. ..	Wind W. Rain from 10 A.M. to 11.30 A.M.	60·0°	57°	29·85
12 noon	Cloudy	57·0	56·0	"
2.0 P.M.	"	60·0	59·0	"
3.0 "	Sky clear. Sun shining ..	65·0	65·0	"
4.0 "	" " ..	64·0	62·0	"
5.0 "	" " ..	65·0	64·0	"
6.0 "	" " ..	63·5	63·0	"
8.0 "	"	57·0	56·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per	100,000	grains.
Before experiment	0·482	0·526	0·192	1·48
After experiment	0·172	0·264	0·121	1·44
Results of one mile flow	— 0·310	— 0·262	— 0·071	— 0·04

Experiment 4 (July 4th).

Water employed in Experiment.—New River water, containing 8·83 per cent. (1 in 12) of sewage.

Quantity Experimented on.—Six gallons.

Distance of Travel and Time occupied in the Experiment.—One mile in 9·5 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
10. 30 A.M. . .	Sun and cloud. West wind	65 ·0°	61 ·0°	30 ·1
12. 0 noon . . .	" " "	67 ·0	64 ·0	"
1. 0 P.M. . . .	" " " " " "	69 ·0	63 ·5	"
2. 0 " " " "	" " " " " "	70 ·0	65 ·0	"
3. 0 " " " "	" " " " " "	71 ·0	62 ·0	"
4. 0 " " " "	Bright sun " " " "	71 ·5	68 ·0	"
6. 0 " " " "	" " " " " "	69 ·5	65 ·0	"
8. 0 " " " "	" " " " " "	64 ·0	62 ·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per	100,000.	grains.
Before experiment . . .	0 ·538	0 ·673	0 ·203	1 ·584
After experiment	0 ·187	0 ·286	0 ·071	1 ·54
Results of one mile flow	— 0 ·351	— 0 ·387	— 0 ·132	— 0 ·044

NOTE.—The dust was excessively troublesome during the day.

Experiment 5 (August 15th).

Water employed in the Experiment.—New River water, containing 4 per cent. of sewage.

Quantity Experimented on.—Fifty pints.

Time of Travel occupied and Distance.—One mile in 8 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water. (Fahr.).	Bar. pr. inches.
12. 0 noon . . .	Sun bright. Wind S.W.	70 ·0°	66 ·0°	29 ·4
1. 0 P.M. . . .	" " " " " "	72 ·0	65 ·0	"
2. 0 " " " "	Cloudy " " " " " "	70 ·0	64 ·5	"
3. 0 " " " "	Heavy shower between 2 and 3, lasting 10 minutes	66 ·5	63 ·0	"
4. 0 " " " "	Fine. Sun shining	70 ·0	65 ·0	"
5. 0 " " " "	" " " " " "	67 ·5	65 ·0	"
6. 0 " " " "	" " " " " "	65 ·0	62 ·0	"
7. 0 " " " "	" " " " " "	64 ·5	60 ·0	"
8. 0 " " " "	" " " " " "	63 ·0	59 ·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per 100,000.		grains.
Before experiment.	0·280	0·358	0·140	1·46
After experiment.	0·086	0·184	0·070	1·40
Effects of one mile flow.	— 0·194	— 0·174	— 0·070	— 0·04

Experiment 6 (August 16th).

Water Employed in the Experiment.—New River water, containing 4 per cent. of sewage.

Quantity Experimented on.—Fifty pints.

Time and Distance.—One mile in 6 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
11 A.M.	Fine. Sun shining	63·5°	62·0°	29·3
12 noon	Dull	66·0	61·5	..
Experiment was here interrupted for 2½ hours, on account of a heavy storm, succeeded by frequent showers.				
3.0 P.M.	Dull	62·0°	60·5°	29·3
4.0 "	"	64·0	61·0	"
5.0 "	Fine. Sun shining	65·0	62·0	"
6.0 "	"	61·0	60·5	"
7.0 "	Cloudy	59·0	57·0	"
8.0 "	"	59·0	56·5	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per 100,000.		grains.
Before experiment, as in previous experiment	0·280	0·358	0·140	1·46
After experiment	0·064	0·163	0·06	1·24
Results of one mile flow	— 0·216	— 0·195	— 0·080	— 0·22

NOTE.—This experiment was not very satisfactory, as there is little doubt but that some rain got into the apparatus, the showers at intervals being very heavy.

Experiment 7 (August 17th).

Water Employed in Experiment.—New River water containing 1 per cent. of London sewage.

Quantity Experimented on.—Fifty pints.

Time and Distance.—One mile in 8 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
10 A.M.	Fine. Wind W....	62·0°	60·4°	29·8
11 "	"	64·0	61·0	"
12.0 noon	"	63·0	60·4	"
1.0 P.M.	"	65·5	62·0	"
3.0 "	"	66·5	62·0	"
4.0 "	"	70·0	67·0	"
5.0 "	"	66·0	62·0	"
6.0 "	"	63·0	60·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per 100,000		grains.
Before experiment	0·075	0·175	0·054	1·26
After experiment.....	0·051	0·132	0·04	1·30
Result of one mile flow.	— 0·024	— 0·043	— 0·014	+ 0·04

Experiment 8 (August 18th).

(Duplicate of last Experiment).

Water Experimented on.—New River water containing 1 per cent. of sewage.

Quantity Experimented on.—Fifty pints.

Time and Distance.—One mile in 9 hours.

Time.	Weather.	Temperature of air (Fahr.).	Temperature of water (Fahr.).	Bar. pr. inches.
1 P.M.	Very fine day. Wind N.E.	72·5°	67·0°	29·8
2.0 "	"	73·0	68·0	"
3.0 "	"	71·0	68·0	"
4.0 "	"	69·0	67·0	"
5.0 "	"	68·5	67·0	"
6.0 "	"	65·0	63·0	"
7.0 "	"	64·0	62·0	"
8.0 "	"	63·0	61·0	"
9.0 "	"	61·0	60·0	"
10.0 "	"	59·0	58·0	"

Analysis.

	Oxygen required.	Organic C.	Organic N.	Chlorine.
	grain.	part per 100,000		grains.
Before experiment	0·073	0·184	0·050	1·26
After experiment	0·046	0·121	0·041	1·28
Result of one mile flow.	— 0·028	— 0·063	0·009	+ 0·02

Throughout my experiments I employed New River water mixed with different proportions of sewage, except in the experiment marked No. 1 in the tables, where I operated on New River water unmixed. As a rule the time occupied by each experiment was eight hours; but inasmuch as not more than one-fifth of the total volume of water was flowing through the troughs at any given time, and there was frequently some slight delay in the pumping operations, I think it may be estimated that the flow was at the rate of about one mile in $1\frac{1}{2}$ hours. It may at times have been a little more or a little less than I have stated, but this may be taken as an average. At any rate, in all the experiments, whatever the time occupied may have been (*i.e.*, whether it was $1\frac{1}{2}$ hours or $1\frac{3}{4}$ hours, and these I should think were the extreme limits), the water employed had a run of one mile.

The sewage used was, except in one or two cases, filtered London sewage taken from Abbey Mills pumping station. The quantity employed throughout was about six gallons. It was measured accurately before the experiment commenced, the loss by evaporation being made up with distilled water at the conclusion of the experiment.

A sample was examined in each case, before and after the mile run, for organic carbon and nitrogen. The oxygen required to oxidise the organic matter and the chlorine were also estimated, this latter being determined mainly as a check on the loss by evaporation.

In the tables I have also recorded the state of the weather, the temperature both of the air and of the water, and the barometric pressure hourly during the progress of the experiment.

In the first experiment, where New River water alone was used, the carbon and nitrogen decreased after the mile flow 0·027 part per 100,000, the oxygen required being less by 0·011 grain.

In the second experiment, with 5·5 per cent. of sewage, the organic carbon and nitrogen decreased 0·218 part, and the oxygen required was less by 0·210 grain.

In the third experiment, with 6·6 per cent. of sewage, the organic carbon and nitrogen was less by 0·313 part, and the oxygen by 0·310 grain.

In the fourth experiment, with about 8·3 per cent. of sewage, the organic carbon and nitrogen were less by 0·519 part, and the oxygen by 0·351 grain.

In the fifth experiment, with 4 per cent. of sewage, the organic carbon and nitrogen were less by 0·244 part, and the oxygen by 0·194 grain.

In the sixth experiment, again with 4 per cent. of sewage, the organic carbon and nitrogen were less by 0·275 part, and the oxygen by 0·216 grain.

In the seventh experiment, with 1 per cent. of sewage, the organic carbon and nitrogen were less by 0·057 part, and the oxygen by 0·024 grain.

In the eighth experiment, again with 1 per cent. of sewage, the organic carbon and nitrogen were less by 0·072 part, and the oxygen by 0·028 grain.

I do not wish it to be understood that these were all the experiments made. It is true they were the successful ones, but the success in others was so manifestly due to difficulties with which we had to contend, such as dust and soot, that it would be waste of space, I think, to record them.

One circumstance was always noted, whatever analysis had to show, viz., that after two or three runs through the apparatus, and sometimes with only a single run, the offensive smell of the sewage water had disappeared. The change indeed in this respect was most remarkable.

It was further evident that the last traces of the organic matter were the most difficult to oxidise. The first part rapidly disappeared, but as the organic matter in the water lessened, rapidity of oxidation decreased. But of course it must be remembered that our experiments were only comparable with river water in the matter of run. They were not entirely comparable even in this respect, seeing that we had a smooth lining to our troughs, whilst in rivers there is usually a rough bed. Further, in rivers we have (when a certain purity has been reached) the purifying agency of fish and plants, neither of which played any part in the experiments I have recorded. These circumstances account for a very much less rapid oxidation in the troughs than I believe occurs in rivers.

My conclusions therefore on this subject do not quite agree with those of the Rivers Pollution Commissioners.

"We are led," they say, "to the inevitable conclusion that the oxidation of the organic matter in sewage proceeds with extreme slowness, even when the sewage is mixed with a large volume of unpolluted water, and that it is impossible to say how far such water must flow before the sewage matter becomes thoroughly oxidised. It will be

safe to infer, however, that there is no river in the United Kingdom long enough to effect the destruction of sewage by oxidation." (Sixth Report, p. 138.)

I am, on the contrary, led to the inevitable conclusion that the oxidation of the organic matter in sewage, when mixed with unpolluted water and allowed a certain flow, proceeds with extreme rapidity, and that it is impossible to say how short a distance such a mixture need flow under favourable conditions before the sewage matter becomes thoroughly oxidised. It is certain, to my mind, that there is no river in the United Kingdom but what is many times longer than is required to effect the destruction of sewage by oxidation.

Be it understood I do not question the accuracy of one of Dr. Frankland's experiments. So far from doing so, whenever I have repeated them I have found my results closely agree with his. What I do question are the conclusions he deduces from the results.

From this discussion on Nature's methods of purifying running water, I pass by easy transition to consider what art can effect in a similar direction. But here permit one general statement that must govern all I have to say on this question. The powers of science and art must never be invoked (I hold this emphatically in the matter of a water supply to a community) to deal with a water which is primarily impure. Given an impure source, there is no help that I can see but the entire abandonment of the source. Art may be fairly asked to improve a good water, but it is simple madness to ask her to deal with a bad water. There is no greater evil I am convinced than the system of doctoring waters. If for any reason a water be unsuited for the purpose for which it is wanted, let it be given up, and a new source sought for.

In urging the claims of rivers as one of the sources for water supply, I mean rivers free from sewage,—not necessarily rivers that have never received a trace of sewage (I question whether there is any water in the world absolutely uncontaminated), but rivers the purity of which at the suggested intake can be proved by chemical analysis, and the maintenance of which purity law can demand.

But given this, art can do a great deal. And it appears to me that although exceptions may occur, it may be laid down as a general rule that if river water be used as a supply it must be efficiently engineered.

By efficient engineering I understand storage, subsidence, and filtration.

As regards *subsidence*, its importance depends not merely on throwing as little work as possible on the filter beds, but on the fact that the filtration of a fairly clear water is necessarily always more perfect than when the water is turbid. So far as the chemist is concerned I

have only one remark to make on subsidence, viz., that our knowledge of the rate of subsidence in the case of one river water is no guide to what the rate of subsidence will be in a second. I will take for example four river waters, viz., the Shannon, the Severn, the Thames, and the Mole. Two days' subsidence for Shannon water will be quite as efficient (perhaps even more efficient) than seven days for Severn water, ten days for Thames water, or fifteen days for Mole water. I will not pursue this matter further save to remark, that from an engineering point of view this question is one of the utmost importance (for the remaking of filter beds is no mean item in water-works expenditure), and can be settled only by actual experiment.

I now pass to *filtration*, a process which does not consist merely in the separation of suspended impurities, but by effecting a minute subdivision of the water, reduces, often very largely indeed, the quantity of dissolved organic matter.

And here one word on varieties of filtering material. It will be understood that my remarks apply to filtering a good river water. I am prepared to admit that as regards the best filtering medium there is room for some diversity of opinion. My own experience on different filtering materials is by no means a limited one; further, the experiments I have made have been for the most part conducted on a scale that can scarcely class them with laboratory experiments. I do not purpose for obvious reasons to go into any detail on this question, nor to mention any special materials, although if details were necessary I have no few in my note book; but I have been led from a consideration of all the facts to one conclusion, viz., that having regard to the three particulars of (1) efficiency, (2) permanence, and (3) cost, sand filtration is superior to any other. I am confining my remarks now to filtration on a large scale, with no reference whatsoever to domestic filtration. I admit there are materials which for a time (and oftentimes a very limited time indeed) yield better results than sand; but as in practice *permanence* of action must be considered simultaneously with *excellence* of result, it is clear that a material, however well it may filter for a short period, which cakes and after a time refuses to work, cannot be recommended. Nor indeed must we altogether ignore the question of cost, although I admit it to be of very inferior importance; but as regards efficiency and permanence, I believe sand properly used, not merely to be perfectly efficient, but also to be singularly permanent.

But in the matter of sand filtration I am anxious to direct attention to four practical points.

1. *The kind of sand employed.* This is most important. As regards *quality* it should be a *pure* sand, i.e., it must not be a felspathic sand or a sand containing decomposed felspar (kaolin). But besides quality,

the size of the particles is a matter demanding the utmost attention. They should not be too small nor too large, but of medium size. But what is more important even than size *per se*, is uniformity of size. The reasons for this are obvious. If you have a sand made up of particles of every conceivable size, the heap when placed *en masse* is practically solid, the medium sized pieces occupying the spaces left by the larger pieces, and the smallest pieces the spaces left by the medium sized pieces. Thus practically no spaces at all remain. But if the particles be as nearly as possible of the same size, it is manifest that spaces between the particles must result, and to such an extent that the air spaces—as I have proved by experiment—will be almost equal to the space covered by the actual sand. This state of things, viz., a pure siliceous sand, the particles being uniformly of medium size, constitute, according to my results, the perfection of a filter bed.

2. But sand after it has been used for some time requires rewashing. I have had opportunities on many occasions at different waterworks to examine the results of sand washing by different processes and methods, and I make this general observation, that so far as my experience goes, much of the dissatisfaction that has arisen with regard to river water has been due to imperfect filtration through imperfectly washed sand. The operation of washing sand is a most delicate one, and on the perfection of that washing will depend, in a great measure at least, the purity or impurity of the filtered water. I have before me a long series of experiments showing the relationship between the organic matter in the unfiltered and in the same water after filtration through sands of various degrees of purity, and the results show conclusively how important a matter is the purity of the sand. I somewhat hesitate in fixing a definite standard of purity to which sand should be brought before it is laid down, or a standard of impurity it should be allowed to attain before it is taken up to be rewashed. The perfect apparatus for washing sand that is used at certain waterworks in the eastern counties, where in my opinion sand washing is as nearly as possible brought to perfection, shows what can be done by careful attention to this matter. I will on this question content myself with laying down two rules:—

(α .) That the apparatus used should be such that the cleansing of the sand is complete, the operation itself being conducted as rapidly as possible.

(β .) That the water used for at least the final rinsing of the sand should be the best filtered water attainable.

3. As regards *rate of filtration*, the thing to be sought for is “the happy medium.” My results show that both too rapid or too slow filtration is to be avoided, but of the two, a too rapid filtration is pre-

ferable to a too slow filtration. Without troubling the Society with a large number of experiments on this point, I will only say this much, that I am convinced the more nearly the rate of filtration approaches two gallons per square foot of filtering surface per hour the better is the filtrate. And here I may explain that in using the terms better and worse, I mean judged by a comparison between the dissolved organic matter in the filtered and the unfiltered water. As regards actual rate, however, much will depend on the thickness of the filter bed.

4. *The life of a filter bed* is a subject on which much could be said if time allowed. A *first* short period of inefficient filtration, a *second* period of efficient filtration, a *third* period of very inefficient filtration, and a *fourth* period where the filter bed begins to work fairly well again, are the four periods in its life that can be plainly recognised by the examination and analysis of the filtered waters, and the analysis of the sand at different depths from the surface. Without pursuing this tempting question, I will say this, that no sand filter used for filtering river water can be expected to work efficiently (*i.e.*, as efficiently as a sand filter can be made to work) for an indefinite period, and that most careful experiments have convinced me that two years is about the active period of its life, after which the whole of the sand needs rewashing. And of course I am supposing that even during this two years constant attention is given to removing the top-most inch or so of the filter bed, and replacing the same by well washed sand.

III.—*I have now to consider how far statistics warrant us in condemning or in approving the supply of river water for drinking purposes.*

I confess to feeling some difficulty in venturing to discuss a question of this nature before the Chemical Society. It would, I admit, seem more fitting for the deliberations of a medical society. My apology must be that every water analyst is expected to give an opinion, founded on the results of his examination, whether the water submitted to him be wholesome or otherwise. Further, in the most recently published *Manual of Water Analysis* (the appearance of which we must all hail with satisfaction), the learned author has thought it right to give hints for the interpretation of results. If, as a medical man, I venture to transgress a little the bounds of pure chemistry, I can only plead that in my humble judgment everything that concerns the practice of chemistry should be a subject of discussion amongst chemists.

On the question of the unwholesomeness or otherwise of peat in water I will only say one word. It is generally stated to cause diarrhoea. *A priori* argument would certainly lead one to say that the

action of peat, if it has any action at all, would be that of an astringent. I admit that in certain Irish towns supplied with peaty water (and I have had occasion of late to go into this matter in some detail) the death-rate from diarrhoea is excessive, by that I mean above the average diarrhoea death-rate of England; but it is also true that in certain other towns supplied with equally peaty waters (and in one case more peaty probably than all the rest) the diarrhoea death-rate is below the average. It may further be worth noting, as shown in Table XV, that the diarrhoea death-rate (calculated on the statistics of ten years), of districts supplied with river water (which always contains some peat), is 0.86 per 1,000, whilst in the districts supplied with well waters, most of which are absolutely free from peat, the diarrhoea death-rate during the same period was 1.12 per 1,000. From these and many other facts, with which I do not purpose troubling the Society, I am led to conclude that the notion that a peaty water causes diarrhoea is scarcely borne out by the facts.

Leaving peat, and coming to the far most serious matter of animal pollution, I am quite aware of the difficulty that will be raised and is in store for me. Admit it may be said that organic matter is oxidised in the course of a river flow; how about organised bodies? Dr. Frankland has stated this case so clearly in a remarkable answer he gave upon one occasion to a question put to him by a learned counsel in a celebrated Parliamentary case, that I quote it word for word:—

“Suppose you throw into the Thames at Oxford a quantity of albumin, which is the white of egg, and we will suppose that you put into the Thames at the same time a living fish, and they both come down by the stream towards London, the fish would reach London unaltered, a little bit increased in size perhaps, and the albumin would have undergone the process of oxidation to a certain extent? What I mean to say is, that if there are living matters in the sewage, they will pass down a great stretch of the river without oxidation.”

The argument conveyed in this answer, if I understand it aright, amounts to this:—suppose we admit that the organic matter of the sewage is oxidised during the flow of a river, what becomes of the germ? And here unfortunately we leave the region of direct experiment, and are plunged headlong into theories.

I am anxious not to be misunderstood. That disease may be caused by drinking impure and polluted water—and indeed I will go further, and say that impure water has been one of the most active causes of disease—is a fact which to my mind has been proved beyond doubt. The researches of Dr. Ballard at Islington on typhoid caused by the admixture of polluted water with milk, the Caterham outbreak, the numerous cases of disease resulting from drinking impure surface well water, supply evidence that should make us very jealous indeed of

allowing a water to be used for drinking over which hangs the merest shadow of a suspicion. No one can be too strictly a water purist.

But in the case of a river water, the argument against its use is based *first*, on the existence of germs, and *secondly*, on the supposition that the oxidation process which might affect organic matter would probably leave organised bodies untouched.

I do not propose discussing the truth or untruth of the germ theory. Admitting that recent investigations have proved in certain cases, notably in remittent fever, in splenic fever, and in pig typhoid, the existence of certain organisms, which organisms have the power, when introduced into the circulation of a healthy animal, of inducing a disease similar to that existing in the animal from which they were derived, we are led to inquire into the conditions of their life. As yet the existence of germs as the cause of typhoid, of cholera, and so on, being hypothetical, we do seem to be diving deeper and deeper into mere speculation when we discuss the laws governing the life of organised bodies, the very existence of which at present is unproved. But the question for us is this:—admit germs of disease finding their way in sewage into a river, is there any evidence, chemical or otherwise, to indicate that these germs are not amenable to the same laws to which organic matter generally is amenable? Admit them to be organised cells; at any rate are they not so low in the scale of life that they may fairly be regarded as occupying a transition space between the organic and the completely organised? Or again, admit these germs being poured along with the sewage into a river and subjected to a flow of 10 or 12 miles, would they not in all probability, arguing by analogy, very soon suffer complete destruction by the bursting of their envelopes owing to the powerful endosmic action of the water in which they are immersed? Surely a river is not their natural element. Admit the germ theory, and is not this endosmic action the probable explanation of the purifying influence of a shower of rain?

But we have the means of going one step further in our investigations. That one step is the appeal to statistics. Again, I say admit germs as the *materies morbi*—these germs must either be subject to the ordinary laws to which organic matter generally is subject, or if not so, they must be governed by the laws of organised bodies (like fish in fact), that is, they ought to increase, and every town as we pass down a river supplied by the river water, should clearly exhibit a constantly increasing death-rate from the special disease. One typhoid fever patient may, it is held by the advocates of the germ theory, produce an endless quantity of typhoid germs, each germ I suppose being capable of becoming a disease producer. Is there any evidence whatsoever of this enormous increase in zymotic cases? Statistics show a

very different state of things. Strange to say, it will invariably be found, as a question of time, that the progress of such a disease as cholera is not *down* a river at all (as we should expect it to be), but in the opposite direction.

Again, let us compare the statistics of death in towns supplied by river water, with those of towns supplied by deep well and spring waters. I have devoted much time to this question, and in the endeavour to obtain a large body of facts upon which to draw some conclusions, I have taken the statistics for 10 years of 18 towns supplied by well and spring water, to compare with the same 10 years' statistics of 18 towns supplied by river water. My results are stated in Table XV.

TABLE XV.

Showing the average death-rate, and the number of deaths, &c., from various diseases during 10 years in 18 towns supplied by deep well or spring water, and in 18 towns (omitting London) supplied by river water.

	Estimated population.	Average death-rate.	Diphtheria.	Fever.	Diarrhoea.	Cholera.	Disease of kidneys.
18 towns supplied by wells.	889,340	22·72	1,508	7,549	9,982	632	2,851
18 towns supplied by rivers.	911,742	22·66	1,329	8,321	7,900	1,046	2,811

TABLE deduced from the above, showing the deaths per year from the several causes per 1,000 of the estimated population.

	Diphtheria.	Fever.	Diarrhoea.	Cholera.	Disease of kidneys.
18 towns supplied by wells.	·1695	·8488	1·1223	·0710	·3205
18 towns supplied by rivers.	·1457	·9126	·8664	·1147	·3083

These details, which, let me add, have been tested in a variety of ways, are remarkable. The 18 well towns had an estimated population of 889,000, and the 18 river towns a population of 911,000. In population therefore they were closely comparable. The well towns had an average death-rate of 22·72 per 1,000, and the river towns a death-rate of 22·66, a difference of 0·06 in favour of rivers as a water supply over wells. Analysing the details, wells have the advantage in deaths from fever in the proportion of 8·488 per 1,000 against 9·126 per 1,000

in the case of rivers. Similarly in the case of cholera, wells stand before rivers in the proportion of 0·710 deaths per 1,000 in the well towns against 1·147 in river towns. On the other hand, river towns show to advantage in diphtheria, 1·457 deaths per 1,000 being registered in river towns against 1·695 in well towns. The difference is most remarkable in the case of diarrhoea, for in river towns 8·644 deaths per 1,000 are recorded, whilst in well towns we have an average of 11·223 deaths per 1,000. It is worthy of note in passing, that deaths from diseases of the kidneys are as nearly as possible alike in both.

At any rate these statistics, as they are on a very extensive scale, prove tolerably conclusively, it appears to me, that there is no evidence to show any manifest difference in the matter of health between towns supplied by wells and those by rivers.

Let me now attempt to narrow our investigations a little. I have purposely omitted London from the statistics I have already quoted, but it is worth while to examine a little closely the metropolitan death statistics. Five companies it is well known supply London with filtered Thames water, one with Lea water, one with a mixture of Thames and Lea water, one with a mixture of Lea water and spring water, and

TABLE XVI.—*London Water Supply and Health Statistics, compiled by Mr. Baldwin Latham, C.E., F.G.S., &c.*

Year.	Proportion of organic impurity in Thames water as delivered in London.	Proportion of organic impurity in Lea water as delivered in London.	General death-rate of London.	All zymotic diseases death-rate of London.	Fever death-rate of London.	Diarrhoea death-rate of London.	Death-rate per 1,000 living at ages from 0 to 5 years.	Death-rate per 1,000 living at ages from 5 to 20 years.
1868	1,000	484	23·5	6·0	0·78	1·28	80·6	5·8
1869	1,016	618	24·6	6·6	0·78	1·07	86·0	6·6
1870	795	550	24·1	6·2	0·68	1·17	79·5	6·8
1871	928	604	24·6	7·0	0·53	1·19	78·6	7·1
1872	1,243	819	21·5	4·9	0·40	1·05	70·9	4·8
1873	917	693	22·5	4·5	0·46	1·15	71·6	4·4
1874	933	583	22·6	4·5	0·46	0·92	70·9	5·2
1875	1,030	751	23·8	5·1	0·37	0·92	77·7	5·7
1876	903	562	22·2	4·7	0·33	1·00	72·8	5·0
1877	907	596	21·9	4·5	0·35	0·70	69·2	5·3
1878	1,056	747	23·5	5·1	0·38	1·02	78·3	5·4
Totals	10,728	7,007	254·8	59·1	5·47	11·47	836·1	62·1
Average	975	637	23·1	5·3	0·49	1·04	76·0	5·6

In 1872 with the greatest amount of impurity all deaths are below the average.

In 1870 with the least amount of impurity all deaths are above the average.

one with water from deep chalk wells. Of course the river water in some years, so far as organic impurity is concerned, is better than in others. Dr. Frankland's and my own results on this point closely agree. I am indebted to Mr. Baldwin Latham for the foregoing remarkable table (Table XVI), in which he has tabulated the quantity of organic impurity in the Thames and Lea, as reported by Dr. Frankland for 11 years, year by year, from 1868 to 1878 inclusive, stating in corresponding columns the general death-rate of London, the death-rate from all zymotic diseases, the fever death-rate, and the diarrhoea death-rate for each year. It certainly is remarkable that in 1872, when Dr. Frankland reports the greatest amount of organic impurity in the river water, we have the lowest recorded death-rate, the diseases mentioned, excepting diarrhoea, also being in every case below the average. Equally remarkable is it that in 1870, when the least amount of organic impurity in the Thames and Lea is recorded, the death-rate and the various deaths from the special diseases are all above the average. I am aware that the death-rate appears to follow almost an inverse proportion to the quantity of water in the Thames, the larger the quantity in the river the less the death-rate, but this point I cannot stay to discuss, most suggestive though it be.

Once again we have in London certain places supplied with river water, a second series supplied with deep chalk water, and a third series supplied with a mixture of river and chalk water. It is worth our while to compare the death statistics of these districts one with another. Again I am indebted to Mr. Baldwin Latham for the following table (Table XVII), the details of which I have myself verified. (1) Lambeth and Wandsworth have been selected as districts supplied with river water only, by the Lambeth and the Southwark and Vauxhall Water Companies; (2) Greenwich and Woolwich, as fairly comparable districts, supplied entirely with chalk water by the Kent Water Company; and (3) Camberwell and Lewisham have been taken as districts supplied partly by a company deriving their supply from a river (both the Lambeth and the Southwark and Vauxhall in the case of Camberwell, and the Lambeth only in the case of Lewisham) and partly with chalk water. The average of 10 years has been taken, and the results show that the death-rate from all causes in the river districts and the death-rate in the well districts are practically identical, whilst the death-rate of those districts receiving a mixed supply is manifestly less than either. But what is more remarkable still is, that the death-rate from enteric fever, from scarlatina, from diarrhoea, from diphtheria, and from dysentery, is in each case slightly lower in the districts supplied with river water than in the districts supplied with well water, whilst so far as cholera is concerned the returns in both are identical.

TABLE XVII.—Tables showing the Average Rates of Mortality per Thousand of the Population for the Ten Years 1868 to 1877, in the several Districts in London and the Neighbourhood. Compiled by Mr. Baldwin Latham, C.E., F.G.S., &c.

Name of district.	Source of water supply.	Birth-rate.	Death-rate.	Pneumonia death-rate.	Fever death-rate.	Enteric-fever death-rate.	Scarlatina death-rate.	Diarrhoea death-rate.	Cholera death-rate.	Diphtheria death-rate.	Dysentery death-rate.	Estimated population, 1877.
Lambeth.....	Lambeth, and Southwark and Vauxhall Water Companies } Southwark and Vauxhall, and Lambeth Water Companies }	38.55	23.30	2.46	0.61	0.32	0.92	1.00	0.05	0.13	0.02	229,190
Wandsworth		36.02	19.85	2.04	0.41	0.20	0.83	0.93	0.05	0.12	0.02	169,890
		74.57	43.15	4.50	1.02	0.52	1.75	1.93	0.10	0.25	0.04	
		Totals.....										
	Average.....	37.28	21.57	2.25	0.51	0.26	0.87	0.96	0.05	0.12	0.02	
Greenwich	Kent Water Company Kent Water Company Totals..... Average.....	37.65	22.76	2.53	0.53	0.27	0.81	1.05	0.04	0.10	0.09	110,920
Woolwich		37.38	20.21	2.63	0.54	0.27	0.98	0.93	0.06	0.19	0.03	74,000
		75.03	42.97	5.16	1.07	0.54	1.79	1.98	0.10	0.29	0.12	
		Average.....	37.51	21.48	2.58	0.53	0.89	0.99	0.05	0.14	0.06	
Camberwell.....	Lambeth, Southwark and Vauxhall, and Kent Companies (Kent Company in part of Peckham) Lambeth and Kent Water Companies Totals..... Average.....	36.20	20.73	2.18	0.41	0.21	0.77	0.97	0.07	0.09	0.03	150,650
		31.42	15.82	1.60	0.27	0.19	0.67	0.67	0.02	0.14	0.01	64,000
		67.62	36.55	3.78	0.68	0.40	1.44	1.64	0.09	0.23	0.04	
		Average.....	33.81	18.27	1.89	0.34	0.72	0.82	0.04	0.11	0.02	
London mortality		35.70	23.13	2.65	0.49	0.26	0.86	1.03	0.05	0.11	0.02	3,533,454

Surely these facts (1) that the death-rates of well towns and river towns are practically alike, and (2) that in the metropolis there is very little to choose, judged by mortality, between districts supplied with well water, and those supplied with river water, any slight difference being in favour of water from the river, justify this conclusion, that be the *materies morbi* what it may, organised matter or chemical poison, it is subject to the same laws of destruction as the ordinary organic matter in sewage. I do not wish to hide the fact that, as a matter of sentiment, if two schemes of water supply were placed before me, the one from a river and the other from springs or deep wells, I should unhesitatingly, purity being equal, choose the latter. But convinced that there are good and bad rivers and good and bad wells, the professional adviser's duty is plainly this: to judge every scheme of water supply on its own merits, and to support that scheme only (be it river or well) which, having regard to quantity, is chemically the purest and the most likely therefore to be wholesome.

In urging these views I am contending practically for the importance of water analysis. It does appear to me that if you once admit that organic matter may be oxidised or otherwise disappear, but that the undiscoverable germ, the cause of all the mischief, may all the while remain in the water intact, a certain terrible doubt is cast over any opinion we may base on the analytical results, and, which doubt, as a chemist, I cannot allow. In fact, if such a view be true, I fail to understand the value of water analysis at all. Admit on the other hand that the *materies morbi* disappears together with the disappearance of the organic pollution (as I contend facts prove), it is manifest that the chemist is strengthened when he pronounces a water wholesome and fit to drink. I may here ask two questions: *first*, has there ever been a well-authenticated case where river water, having received sewage, dilution being considerable and circumstances favourable for oxidation, has, after a flow of 10 or 12 miles, been manifestly the cause of an outbreak of disease? I know of none. *And this next*: has there ever been a well-proved case of an outbreak of disease, resulting from the use of drinking water, where the chemist would not unhesitatingly on analysis have condemned the water as an impure source? Again, I know of none.

One thing is certain; this subject, "of vital importance," as Dr. Frankland calls it, must be discussed on the facts and not as a matter either of sentiment or of fashion. I am conscious that I am on the unpopular side; still one cannot help noting that so far as *fashion* is concerned, since Dr. Ballard's magnificent enquiry at Islington, the admixture of milk with polluted water is the now invariably ascribed cause of all typhoid outbreaks. And, so far as *sentiment* is concerned, I will read one paragraph only from the Sixth Report of the Rivers

Pollution Commissioners. I quote it as it stands, absolutely unqualified by a single word preceding or following it. Speaking in justly laudatory terms of the deep well water of the Kent Water Company, the Commissioners make this remarkable statement (p. 275, four lines from bottom): "*The supply of such water (i.e., deep well water) to the metropolis generally would be a priceless boon, and would at once confer upon it absolute immunity from epidemics of cholera.*" I ask, do facts warrant that bold promise? We who are aware how little is known of the cause of such epidemics, how they come amongst us when we least expect them and when we think our defences the most secure, how little able we are to cope with them when they are in our midst, may fairly stand surprised when those outside our profession, who have never had the battles we have had to fight with the disease, have committed to paper such a startling promise as "absolute immunity."

Reviewing all the facts I submit the following conclusions:—

1. That when sewage is discharged into running water, provided the primary dilution of the sewage with pure water be sufficient, that after the run of a few miles, the precise distance of travel being dependent on several conditions, the removal of the whole of the organic impurity will be effected.

2. That, whatever may be the actual cause of certain diseases, *i.e.*, whether germs or chemical poisons, the *materies morbi* which finds its way into the river at the sewage outfall, is destroyed together with the organic impurity after a certain flow.

XXI.—*On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State.*

By T. E. THORPE, Ph.D., F.R.S.

(Continued from p. 225.)

Silicon Tetrachloride, SiCl₄.

PREPARED by heating a mixture of pure precipitated silica and lamp-black (previously ignited in chlorine) in a current of dry chlorine gas. The product was repeatedly distilled over sodium. It boiled constantly between 58° and 58·3°, the greater portion coming over at 58·2°. $n = 0$, $t = 0$. Bar. 765·35 mm. Corrected and reduced boiling point 57·57°.

Its specific gravity at 0° compared with water at 4° is 1·52408.

Other observations on record are—

	Boiling point.	Bar.	Specific gravity.	Compared with water at 4°.
Pierre	59·0° at 760·1 mm. (from vapour tension determinations)		1·52371 at 0°	1·52371 at 0°
Regnault	56·81° at 760·0 mm.		—	—
Haagen	58·0 „ 756·0 „		1·4878 at 20°	1·52644 „
Mendelejeff [P] ...	—	—	1·50068 at 10·98°	1·52266 „
Mendelejeff	—	—	1·4928 „ 15°	1·52230 „

The following observations were made in Dilatometer B:—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	2852·7	2852·7	31·61	2978·4	2978·4
6·25	2876·2	2876·1	36·81	3000·8	3000·7
10·50	2892·6	2892·6	42·09	3023·7	3023·8
15·81	2913·6	2913·4	47·57	3048·4	3048·3
20·95	2934·4	2934·1	52·36	3070·0	3070·1
26·25	2955·7	2955·9	57·44	3093·8	3093·7

These observations may be represented by the formula—

$$2852\cdot720 + 3\cdot706\,398t + 0\cdot008\,468\,05t^2 + 0\cdot000\,000\,940\,875t^3,$$

which affords the numbers seen in the third column of the preceding table.

A second series of observations was made in Dilatometer C, with the following results:—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0·00	2960·4	2960·2	31·63	3091·0	3091·1
6·25	2984·8	2984·8	36·81	3114·4	3114·2
10·50	3001·8	3001·9	42·10	3138·2	3138·2
15·81	3023·7	3023·6	47·57	3163·8	3163·6
20·95	3045·2	3045·1	52·37	3186·1	3186·3
26·25	3067·6	3067·7	57·44	3210·8	3210·8

These numbers afford the following formula:—

$$2960\cdot239 + 3\cdot885\,145t + 0\cdot007\,653\,974t^2 + 0\cdot000\,011\,378\,46t^3,$$

which gives the volumes contained in the third column of the table.

Dividing through by the first terms, and correcting for the expansion of the glass, these formulæ become respectively—

$$I. \quad V = 1 + 0\cdot001\,324\,75t + 0\cdot000\,003\,001\,54t^2 + 0\cdot000\,000\,000\,405\,511t^3,$$

and

$$\text{II. } V = 1 + 0.001\,337\,143t + 0.000\,002\,618\,01t^2 + 0.000\,000\,003\,907\,62t^3,$$

The mean formula is—

$$V = 1 + 0.001\,330\,946t + 0.000\,002\,809\,78t^2 + 0.000\,000\,002\,156\,57t^3,$$

which affords the numbers given in the following table, expressing the relative volumes of silicon tetrachloride at every 5° between 0° and 60°.

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	35	105012	760
5	100673	673	40	105787	775
10	101359	686	45	106578	791
15	102060	701	50	107384	806
20	102776	716	55	108206	822
25	103506	730	60	109044	838
30	104252	746	57.57	1.086346	—

According to Pierre the expansion of silicon tetrachloride may be expressed by the formula—

$$V = 1 + 0.001\,294\,119\,069t + 0.000\,002\,184\,143\,631t^2 + 0.000\,000\,040\,864\,220t^3.$$

which represents a curve differing slightly from that afforded by my observations, as will be seen from the following comparison:—

	10°.	20°.	30°.	40°.	50°.
Pierre ..	101320	102708	104189	105804	107527
Thorpe..	101349	102757	104226	105756	107352

Titanium Tetrachloride, TiCl₄.

I am indebted to Dr. Bedson, of Owens College, for a liberal supply of the pure liquid. On distillation it began to boil at 135.8°; the column rapidly rose to 135.9°, at which point the liquid boiled constantly. $n = 19.9$, $t = 24.5^\circ$. Bar. 752.6 mm. Corrected and reduced boiling point 136.41°.

Its specific gravity at 0° compared with water at 4° was 1.76041. According to Pierre this liquid boils at 136° under a pressure of 762.3 mm., and has a specific gravity of 1.76088 at 0° compared with water at 4°.

The following observations of the rate of expansion were made with Dilatometer C.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2971·0	2970·6	36·93	3078·4	3078·4
12·28	3005·7	3005·8	49·19	3115·6	3115·8
24·72	3041·8	3042·0	61·40	3154·4	3154·2

In the oil-bath :—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
38·55	19·6	38·45	3082·1	53·3	3083·0	3083·0
46·87	21·2	46·85	3106·7	78·0	3108·7	3108·6
64·11	25·1	63·99	3157·4	128·7	3162·5	3162·5
74·09	26·3	74·06	3187·6	158·9	3195·4	3195·4
86·49	27·7	86·64	3225·6	196·9	3237·7	3237·8
98·76	29·6	99·17	3264·3	235·6	3281·7	3281·7
113·43	30·4	113·55	3308·6	279·9	3333·8	3334·4
123·46	32·5	123·66	3341·8	313·1	3373·4	3373·1
135·41	34·7	135·87	3381·8	353·0	3422·1	3421·8

These observations afford the formula—

$$2970.586 + 2.845\ 56t + 0.001\ 431\ 43t^2 + 0.000\ 015\ 205\ 3t^3,$$

which on dividing through by the first term and correcting for the expansion of the glass becomes—

$$V = 1 + 0.000\ 982\ 612t + 0.000\ 000\ 505\ 528t^2 + 0.000\ 000\ 005\ 130\ 52t^3,$$

and this affords the numbers given in the following table. It shows the relative volumes of titanium tetrachloride at every 5° between 0° and 140° .

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	75	107870	568
5	100493	493	80	108447	577
10	100988	495	85	109033	586
15	101487	499	90	109627	594
20	101990	503	95	110231	604
25	102496	506	100	110845	614
30	103007	511	105	111469	624
35	103523	516	110	112103	634
40	104044	521	115	112749	646
45	104571	527	120	113406	657
50	105104	533	125	114075	669
55	105643	539	130	114756	681
60	106188	545	135	115448	692
65	106741	553	140	116155	707
70	107302	561	136·41	1·156467	—

Pierre, who has also observed the thermal expansion of this liquid, finds that its rate may be represented by the formula—

$$V = 1 + 0.000\,942\,569\,004t + 0.000\,001\,345\,793\,937t^2 + 0.000\,000\,000\,888\,044t^3,$$

which gives results agreeing with those afforded by my observations.

	30°.	60°.	90°.	120°.
Pierre	102951	106159	109638	113402
Thorpe.....	102989	106169	109621	113414

Tin Tetrachloride, SnCl₄.

I prepared this liquid by heating pure tin in a current of dry chlorine, and expelling the dissolved gas by repeated distillation in a stream of dry carbon dioxide. The liquid boiled very constantly at 113.55°; t 24.5; $n = 6.5$. Bar. 750.8 mm. Corrected and reduced boiling point 113.89°.

Its specific gravity at 0° compared with water at 4° was found to be 2.27875. Other observers have found—

	Boiling point. Bar.	Sp. gr. at 0° compared with water at 4°.
Pierre	115.4 at 753.1 mm.	2.26712
Dumas.....	120 „ 767 „	—
Andrews....	112.5 „ 752 „	—
Haagen	112.0 „ 754.9 „	2.2328 at 20° 2.28137

The following observations of the thermal expansion were made in Dilatometer C.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2961.2	2960.9	40.99	3103.5	3103.3
10.16	2995.0	2995.2	51.14	3140.5	3140.6
20.42	3030.3	3030.5	61.38	3179.5	3179.4
30.84	3066.9	3066.9			

In the oil-bath :—

T°.	t°.	T Δ .	V.	E.	Observed.	Calculated.
72.17	23.1	72.12	3211.1	182.4	3222.1	3221.4
82.44	25.3	82.73	3248.3	219.5	3263.8	3264.5
92.46	28.3	92.69	3286.0	257.3	3307.0	3306.3
102.59	31.2	103.06	3324.3	295.5	3351.5	3351.8
112.67	31.4	112.79	3360.6	331.9	3396.0	3396.2

These observations may be represented by the formula—

$$2960.868 + 3.361\,36t + 0.001\,842\,72t^2 + 0.000\,022\,824\,6t^3,$$

which gives the numbers in the third column of the above table.

A second series made in Dilatometer B gave the following results.

In the water-bath :—

A.	Observed.	Calculated.	A.	Observed.	Calculated.
0.00	2859.6	2859.1	41.00	2996.8	2996.7
10.16	2891.9	2892.3	51.14	3032.5	3032.6
20.42	2926.0	2926.3	61.38	3070.1	3070.1
30.84	2961.5	2961.5			

In the oil-bath :—

T°.	t°.	T ^A .	V.	E.	Observed.	Calculated.
72.18	23.1	72.13	3099.9	188.3	3111.2	3110.7
82.45	25.3	82.74	3135.6	224.0	3151.6	3152.2
92.47	28.3	92.70	3171.6	260.1	3192.9	3192.7
102.57	31.2	103.04	3208.6	297.0	3236.1	3236.4
112.65	31.4	112.77	3243.7	332.1	3279.2	3279.1

These numbers lead to the formula—

$$2859.053 + 3.246\,85t + 0.001\,752\,53t^2 + 0.000\,022\,056t^3.$$

Dividing through by the first terms and correcting for the expansion of the glass, these formulæ become—

$$(I.)\ V = 1 + 0.001\,159\,962t + 0.000\,000\,650\,399t^2 + 0.000\,000\,000\,724\,12t^3.$$

$$(II.)\ V = 1 + 0.001\,161\,138t + 0.000\,000\,641\,935t^2 + 0.000\,000\,007\,730\,07t^3.$$

The mean formula is—

$$V = 1 + 0.001\,160\,55t + 0.000\,000\,646\,167t^2 + 0.000\,000\,007\,727\,1t^3,$$

by the aid of which the following table, showing the relative volume of tin tetrachloride at every 5° between 0° and 115°, is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	108029	666
5	100582	582	70	108706	677
10	101168	586	75	109394	688
15	101758	590	80	110094	700
20	102353	595	85	110806	712
25	102954	601	90	111532	726
30	103561	607	95	112271	739
35	104174	613	100	113024	753
40	104795	621	105	113793	769
45	105424	629	110	114576	783
50	106061	637	115	115376	800
55	106707	646	113·89	1·151971	—
60	107363	656			

Pierre represents the expansion of this liquid by the equation—

$$V = 1 + 0\cdot001\,132\,800\,769t + 0\cdot000\,000\,911\,710\,706t^2 + 0\cdot000\,000\,007\,579\,789t^3,$$

which gives somewhat lower results than those afforded by the mean formula deduced from my observations.

	20°.	40°.	60°.	80°.	100°.
Pierre. . .	102308	104726	107289	110334	112998
Thorpe ..	102347	104771	107341	110080	113024

Phosphorus Trichloride, PCl₃.

This liquid was prepared by heating amorphous phosphorus in a stream of dry chlorine. The red phosphorus of commerce rarely contains more than from 90 to 95 per cent. of that modification of the element, and the ordinary phosphorus with which it is usually mixed gradually oxidises on exposure to air, forming oxy-acids which give the substance an acid reaction and render it hygroscopic. In order to obviate the possible formation of any oxy-chlorides of phosphorus from the presence of these substances, the red phosphorus was placed in a funnel, the neck of which was plugged with asbestos and repeatedly washed with water, afterwards with alcohol, and then with ether, and dried at a gentle heat. The action of chlorine on the heated red phosphorus is very regular, and large quantities of the trichloride may be thus obtained with great ease and rapidity. The product was digested for some weeks with a small quantity of ordinary phosphorus to remove free chlorine and afterwards distilled. It began to boil at 76·05°, and all came over below 76·25°, the larger portion distilling at about 76·15; $n = 18\cdot2$ $t = 26\cdot0$, bar. 768·2 mm.; corrected and reduced b. p. 75·95°.

Two determinations of specific gravity at 0° gave—

I	1·61290
II	1·61299

Mean 1·61294

compared with water at 0°; compared with water at 4° the specific gravity is 1·61275.

Other observations on record are—

	Boiling point.	Bar.	Sp. gr. at 0° compared with water at 4°.
Pierre	78·34°	at 751·5 mm.	1·61616
H. L. Buff ..	76·0	„ 760 „	1·61191 at 0°
Haagen	76·0	„ 745·9 „	1·5774 „ 20°

The following observations of the thermal expansion were made with Dilatometer B:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2855·1	2854·8	44·36	3006·7	3006·6
6·30	2875·2	2875·3	50·76	3030·2	3030·3
12·66	2896·3	2896·3	57·30	3055·0	3055·1
19·01	2917·7	2917·7	63·84	3080·6	3080·5
25·32	2939·0	2939·1	70·28	3106·3	3106·2
31·87	2961·1	2961·9	76·03	3129·5	3129·8

These results may be expressed by the formula—

$$2854·84 + 3·236 \, 18t + 0·003 \, 047 \, 8t^2 + 0·000 \, 025 \, 69t^3,$$

by means of which the numbers in the third column are calculated.

A second series made with Dilatometer C gave—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2972·9	2972·7	44·36	3131·4	3131·1
6·29	2993·8	2994·0	50·75	3155·6	3155·7
12·66	3015·9	3015·9	57·30	3181·2	3181·6
19·01	3038·3	3038·2	63·83	3207·9	3207·9
25·32	3060·5	3060·7	70·31	3234·6	3234·7
31·84	3084·3	3084·3	76·01	3258·6	3258·8

These numbers may be represented by the expression—

$$2972·66 + 3·372 \, 58t + 0·003 \, 575 \, 5t^2 + 0·000 \, 020 \, 81t^3.$$

On dividing through by the first terms respectively and correcting for the expansion of the glass, these formulæ become—

I. $V = 1 + 0·001 \, 159 \, 1t + 0·000 \, 001 \, 096 \, 5t^2 + 0·000 \, 000 \, 009 \, 027t^3$,
and

II. $V = 1 + 0·001 \, 159 \, 2t + 0·000 \, 001 \, 230t^2 + 0·000 \, 000 \, 007 \, 030t^3$.

The mean formula is—

$$V = 1 + 0.001\,159\,2t + 0.000\,001\,163\,7t^2 + 0.000\,000\,008\,029t^3,$$

by means of which the following table, showing the relative volume of phosphorus chloride at every 5^Δ between 0^Δ and 80^Δ , is calculated—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	--	45	105525	651
5	100583	583	50	106187	662
10	101172	589	55	106861	674
15	101768	596	60	107547	686
20	102371	603	65	108247	700
25	102983	612	70	108960	713
30	103604	621	75	109687	727
35	104234	630	80	110429	742
40	104874	640	75.95	1.10827	—

Pierre found that the expansion of phosphorus trichloride might be represented by the formula—*

$$V = 1 + 0.001\,128\,619t + 0.000\,000\,872\,88t^2 + 0.000\,000\,017\,924t^3,$$

which gives results fairly accordant with those calculated from the mean formula obtained from my observations—

	10° .	30° .	50° .	70° .
Pierre	101139	103513	106085	108943
Thorpe.....	101161	103580	106159	108938

Phosphorus Tribromide, PBr_3 .

A quantity of this liquid, prepared by direct synthesis and boiling between 168.5° and 171° , was carefully distilled, and the portion which came over between 169.3° and 170.5° , amounting to about four-fifths of the whole, was collected separately. On redistillation nearly the whole of this fraction boiled between 169.7° and 170.1° ; $n = 95$; $t = 19$; bar. 757.0 mm.; corrected and reduced b. p. 172.9^Δ .

The specific gravity of phosphorus tribromide at 0° , compared with water at the same temperature, was observed to be 2.92349; compared with water at 4^Δ it is 2.92311.

Pierre found the boiling point of this liquid to be 175.3° at 760.2 mm. and the specific gravity 2.92489 at 0° compared with water at 4^Δ .

The following observations were made in Dilatometer C.

* *Ann. Chim. Phys.*, 20 [3], 10. The third term is erroneously printed 0.000 179....

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2955·2	2955·8	43·21	3063·4	3063·4
14·24	2990·2	2990·5	57·56	3100·7	3100·9
28·73	3026·6	3026·5	72·18	3140·3	3140·1

In the oil-bath :—

T° .	t° .	$T\Delta$.	V.	E.	Observed.	Calculated.
72·01	21·1	71·97	3134·2	131·1	3140·0	3140·0
86·76	27·7	86·92	3172·1	169·0	3180·9	3180·9
101·25	31·6	101·71	3210·1	207·0	3223·0	3223·1
115·63	23·2	115·80	3244·4	241·3	3264·6	3264·6
129·89	31·2	130·27	3283·5	280·4	3309·1	3308·6
144·96	38·2	145·68	3325·1	322·0	3357·6	3357·3
158·27	42·6	159·38	3361·6	358·5	3401·4	3401·9

These observations lead to the formula—

$$2955\cdot799 + 2\cdot413\ 165t + 0\cdot001\ 545\ 1t^2 + 0\cdot000\ 005\ 546\ 4t^3,$$

by means of which the calculated volumes in the last columns of the foregoing tables are obtained. It will be noticed that the divergences from the observed volumes are somewhat wider than usual, more particularly at the upper and lower temperatures, but the variations are scarcely sufficient to render it necessary to represent the expansion from 0° to the boiling point by more than one expression.

Dividing through by the first term and correcting for the expansion of the glass ($0\cdot0000247$), the formula becomes—

$$V = 1 + 0\cdot000\ 841\ 17t + 0\cdot000\ 000\ 542\ 892t^2 + 0\cdot000\ 000\ 001\ 889\ 3t^3,$$

by the aid of which the following table, showing the relative volumes of phosphorus tribromide at every 5^Δ between 0^Δ and 175^Δ has been calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	95	108643	495
5	100422	422	100	109143	500
10	100847	425	105	109649	506
15	101275	428	110	110161	512
20	101706	431	115	110679	518
25	102140	434	120	111202	523
30	102577	437	125	111731	529
35	103018	441	130	112266	535
40	103463	445	135	112807	541
45	103912	449	140	113357	549
50	104365	453	145	113913	556
55	104822	457	150	114476	563
60	105283	461	155	115046	570
65	105748	465	160	115622	576
70	106218	470	165	116205	583
75	106693	475	170	116796	591
80	107173	480	175	117395	599
85	107658	485	172.9	—	—
90	108148	490			

Pierre has also determined the expansion of phosphorus tribromide, and has expressed his observations by the two formulæ:—

$$\text{I. } V = 1 + 0.000\,847\,20t + 0.000\,000\,436\,72t^2 + 0.000\,000\,002\,528t^3 \quad (0-100^\circ),$$

and

$$\text{II. } V = 1 + 0.000\,824\,27t + 0.000\,000\,914\,31t^2 + 0.000\,000\,000\,055t^3 \quad (100-175^\circ),$$

which give results agreeing, on the whole, fairly well with those afforded by the single expression deduced from my observations—

	40°.	80°.	120°.	170°.
Pierre	103475	107187	111217	116682
Thorpe.....	103445	107164	111208	116832

Pierre remarks that phosphorus tribromide is characterised by an extremely regular rate of expansion—an observation fully borne out by my experiments.

Phosphoryl Chloride, POCl₃.

Prepared by heating an intimate mixture of phosphorus pentoxide and phosphorus pentachloride in the proportions required by the equation—



The product began to boil at 107°, the greater portion distilling over at about 107.5° (bar. 755.2°). As this boiling point is more than

a couple of degrees below that usually assigned to this compound, I solidified the chloride in a mixture of ice and salt, allowed it to melt partially and poured away the still liquid portion. This operation was repeated several times in the hope that any of the more volatile phosphorus trichloride which might be present would be removed. The boiling point was practically unaltered by this treatment; the liquid distilled completely between 107° and 107.5° , the greater portion boiling at 107.3° under a pressure of 751.0 mm.; $n = 0$; $t = 0$; corrected and reduced b. p. 107.23° .

A second sample, made by heating phosphorus pentachloride with crystallised boric acid, boiled at 107.4° under a pressure of 765.0 mm.; $t = 0$; $n = 0$; corrected and reduced b. p. 107.22° .

The first sample was analysed by breaking bulbs containing known weights of the chloride in a stoppered bottle partially filled with distilled water, and determining the amount of the chlorine in the solution.

Two determinations were made with the following results:—

	I.	II.	
Weight of POCl ₃ , <i>in vacuo</i> ..	1.3156 grams	1.4364 grams	
Weight of AgCl ,, ..	3.6907 ,,	4.1064 ,,	
	I.	II.	Calculated.
Chlorine	69.37	69.39	69.36

Three determinations of specific gravity at 0° made with different bottles gave—

I	1.71185
II	1.71189
III	1.71182
Mean	1.71185

compared with water at the same temperature; compared with water at 4° the specific gravity is 1.71163.

Two series of observations with the dilatometers were made. The first with Dilatometer B gave in the water-bath—:

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0.00	2911.6	2911.5	58.27	3101.9	3102.3
9.78	2941.5	2941.6	67.73	3137.0	3136.4
19.13	2971.1	2971.1	77.43	3172.3	3172.5
29.02	3003.1	3002.9	88.39	3214.9	3214.9
38.73	3035.1	3035.0	95.06	3241.8	3241.6
48.31	3067.1	3067.4			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
68·83	23·6	68·74	3127·3	225·8	3139·1	3139·0
88·33	25·9	88·54	3192·2	290·6	3213·7	3213·6
104·76	30·6	105·29	3250·5	348·9	3283·4	3283·9

These observations lead to the formula—

$$2911·47 + 3·057\ 81t + 0·002\ 674\ 9t^2 + 0·000\ 017\ 823t^3,$$

by means of which the numbers in the last column are calculated.

The second series made with Dilatometer C gave—

In the water-bath :—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	3017·8	3017·6	58·26	3215·4	3215·1
9·78	3048·8	3048·9	67·74	3251·7	3251·2
19·13	3079·4	3079·4	77·44	3288·5	3288·6
29·03	3112·7	3112·5	88·39	3332·4	3332·6
38·73	3146·2	3145·8	95·05	3360·6	3360·1
48·32	3179·1	3179·6			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
104·67	30·6	105·20	3370·3	344·7	3403·1	3403·4

These numbers afford the formula—

$$3017·63 + 3·167\ 52t + 0·003\ 051\ 3t^2 + 0·000\ 016\ 13t^3.$$

On dividing through by the first terms respectively, and correcting for the expansion of the glass, these formulæ become—

I. $V = 1 + 0·001\ 075\ 76t + 0·000\ 000\ 945\ 526t^2 + 0·000\ 000\ 006\ 145t^3$
and

II. $V = 1 + 0·001\ 074\ 37t + 0·000\ 001\ 037\ 09t^2 + 0·000\ 000\ 005\ 369t^3,$

The mean formula is—

$$V = 1 + 0·001\ 075\ 1t + 0·000\ 000\ 991\ 31t^2 + 0·000\ 000\ 005\ 757t^3,$$

by the aid of which the following table, showing the relative volume of phosphoryl trichloride at every 5° between 0° and 100°, is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	60	106932	623
5	100540	540	65	107565	633
10	101086	546	70	108209	644
15	101637	551	75	108864	655
20	102194	557	80	109530	666
25	102758	564	85	110208	678
30	103330	572	90	110898	690
35	103909	579	95	111601	703
40	104496	587	100	112318	717
45	105092	596	105	113048	730
50	105696	604	110	113792	744
55	106309	613	107·23	1·133779	—

The indications of the dilatometers were further controlled by determining the weight of the phosphoryl chloride contained in a specific gravity bottle at 0° and at the temperature of steam from boiling water. The chloride employed was a different preparation from that used in the dilatometers: in fact, the two series of observations were made at an interval of several years with different balances, barometers, &c.; the determinations are therefore in every particular perfectly independent. The mean coefficient of expansion of the specific gravity bottle was found to be 0·00002633. Three observations were made with the following results: the weighings are reduced to a vacuum.

I at 0°	6·55751 grams	at 99·96° (bar. 759 mm.)	5·85339 grams
II „	6·55702 „	99·84 („ 755·5 „)	5·85320 „
III „	6·55708 „	99·74 („ 753·0 „)	5·8535 „

	Volume in ice.	Volume in steam.	Calculated from formula.
I	100000	at 99·96 112292	112311
II	100000	99·84 112287	112296
III	100000	99·74 112281	112282

Considering that the determinations were made with different preparations at different times, and by perfectly distinct methods, the agreement is very satisfactory. The control is the more important in its relation to Matthiessen's remarks on the dilatometrical method of determining thermal expansions.

The specific gravity of phosphoryl trichloride at 10°, 51°, and at its boiling point, has already been determined by H. L. Buff.

The results of his observations, compared with mine for these temperatures, are given below. The specific gravities are compared with water at 0°.

	10°	51°	Boiling point.
Buff	1·6937	1·6494 (? 1·6194)	1·5090 (110°)
Thorpe ..	1·6936	1·6181	1·51008 (107·23°).

Thiophosphoryl Chloride, PSCl₃.

Prepared by the action of phosphorus pentasulphide upon the pentachloride—



The materials were intimately mixed in the proportions required by this equation and heated in a sealed tube at a temperature of about 120°. The reaction is very regular, and large quantities of very pure thioclhoride can be thus obtained. Occasionally the product has a slight yellow colour; if shaken with a little water, and dried by calcium chloride and distilled, it may be readily procured perfectly colourless. Thiophosphoryl chloride boils at 125·0° under a barometric pressure of 760·0 mm.

Corrected and reduced boiling point 125·07^A.

Two determinations of its specific gravity at 0°, compared with water at 0°, gave—

I	1·66815
II	1·66816
Mean	1·66816

A second preparation boiled constantly at 125·5°; $n = 0$; $t = 0$. Bar. 770·0 mm. Corrected and reduced boiling point 125·17^A. Mean boiling point 125·12^A. Two independent determinations made with bottles differing in capacity from those employed in the foregoing observations gave for the specific gravity of the second sample—

I	1·66868
II	1·66864 at 0°.

compared with water at 0°. The mean sp. gr. at 0° compared with water at 4° is 1·66820.

Other observations on record are:—

Mitscherlich	126—127°	
Baudrimont	124—125	1·631 at 22°.

The following observations of the rate of thermal expansion of this liquid were made in Dilatometer B in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2858·6	2858·4	45·39	2990·5	2990·8
11·33	2890·2	2890·4	56·62	3025·8	3025·6
22·42	2922·2	2922·3	68·10	3062·2	3062·3
34·26	2957·4	2957·2			

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
22·54	18·9	22·40	2922·1	35·5	2922·2	2922·2
34·55	20·3	34·42	2956·8	70·1	2957·7	2957·6
45·60	22·1	45·54	2989·0	102·4	2991·5	2991·2
62·39	23·8	62·27	3037·0	150·4	3043·0	3043·5
68·72	25·6	68·63	3056·6	170·0	3064·3	3064·1
79·78	27·3	79·83	3089·6	203·0	3101·0	3101·1
90·88	29·4	91·10	3123·5	236·9	3139·4	3139·5
102·16	31·9	102·65	3158·8	272·2	3180·1	3180·4
113·70	31·6	113·79	3193·0	306·4	3221·3	3221·3
124·12	34·1	124·88	3226·9	340·3	3262·1	3261·6

These observations lead to the formula—

$$I. 2858.375 + 2.797\ 16t + 0.002\ 088\ 15t^2 + 0.000\ 011\ 973t^3,$$

which affords the numbers seen in the last columns of the above tables.

A second series of observations made in Dilatometer C gave the following results. In the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2993·2	2992·7	45·39	3131·4	3131·7
11·33	3026·3	3026·4	56·63	3168·3	3168·2
22·41	3059·7	3059·9	68·10	3206·3	3206·4
34·27	3096·6	3096·6			

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
22·54	18·9	22·40	3059·9	33·1	3060·0	3060·0
34·55	20·3	34·42	3096·2	69·5	3097·2	3097·1
45·61	22·1	45·55	3180·0	103·2	3132·4	3132·2
62·38	23·5	62·26	3180·3	153·6	3186·6	3186·8
68·74	25·6	68·65	3200·7	174·0	3208·7	3208·4
79·77	27·3	79·82	3235·0	208·3	3246·7	3246·9
90·91	29·4	91·13	3270·7	244·0	3287·1	3287·3
102·19	31·8	102·68	3307·7	281·0	3329·7	3330·2
113·71	31·6	113·80	3344·6	317·9	3372·9	3373·0
124·18	34·1	124·44	3379·3	352·6	3416·1	3415·7

From these numbers we obtain the formula—

$$II. 2992.730 + 2.957\ 39t + 0.001\ 591\ 39t^2 + 0.000\ 015\ 741\ 8t^3.$$

Dividing each formula through by its first term respectively, and correcting for the expansion of the glass, we obtain—

I. $V = 1 + 0.00100408t + 0.000000755491t^2 + 0.00000004208t^3$,
and

II. $V = 1 + 0.00101289t + 0.000000556160t^2 + 0.00000005273t^3$.

The mean formula is—

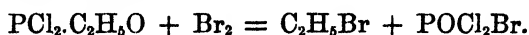
$V = 1 + 0.00100849t + 0.00000065582t^2 + 0.000000047455t^3$,

by means of which the following table, showing the relative volumes of thiophosphoryl chloride at every 5° between 0° and its boiling point is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107544	581
5	100505	505	75	108133	589
10	101015	510	80	108731	598
15	101529	514	85	109337	606
20	102047	518	90	109953	616
25	102570	523	95	110579	626
30	103097	527	100	111215	636
35	103630	533	105	111862	647
40	104169	539	110	112519	657
45	104714	545	115	113187	668
50	105266	552	120	113866	679
55	105824	558	125	114558	692
60	106390	566	125.12	1.145752	—
65	106963	573			

Phosphoryl Bromochloride, POBrCl₂.

I prepared this compound by means of the reaction by which it was first obtained by Menshutkin, *i.e.*, by the addition of bromine to ethoxyphosphorus chloride :—



80 grams of bromine were allowed to fall, drop by drop, into 74 grams of the chloride, which was kept well cooled and constantly shaken. The reaction, which is extremely violent, proceeds in strict accordance with the above equation : direct experiment showed that if the materials be well cooled and slowly mixed, the theoretical quantity of bromine is just needed to colour the liquid permanently orange. As the ethyl bromide boils at about 40° , and the bromochloride nearly 100° higher, the two liquids can be readily separated by distillation.

The bromochloride was found to boil constantly at 136.5° ; $t = 15^\circ$; $n = 108$. Bar. 760.5 mm. Corrected and reduced boiling point 137.6° .

It was analysed by breaking a bulb containing a known weight of the liquid beneath water, acidulating with nitric acid, and precipitating the hydrochloric and hydrobromic acids with silver nitrate.

Weight of bromochloride taken 0.9890 grams

Weight of mixed silver salts 2.3701 „

„ „ (calc.) 2.3720 „

2.3583 grams of the mixed silver salts, heated in a stream of dry chlorine, lost 0.2201 gram: whence we obtain—

	Found.	Calculated.
Bromine	40.05	40.30
Chlorine	35.74	35.83

Two determinations of the specific gravity of phosphoryl bromochloride gave—

I	2.1020 at 8.74 ^A
II	2.1011 at 9.17

compared with water at 4^A. At 0^A, compared with water at 4^A, the specific gravity becomes—

I	2.1206
II	2.1207
Mean	2.12065

Menschutkin found the boiling point 135–137°, and the specific gravity 2.059 at 0°.

The following observations of the rate of expansion of this substance were made in Dilatometer N.

In the water-bath :—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
11.92	3375.8	3375.6	59.55	3539.7	3539.8
26.62	3424.9	3424.9	71.03	3582.2	3582.1
37.55	3462.8	3462.5	84.45	3632.8	3632.7
48.12	3499.2	3499.2			

In the oil-bath :—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
70.50	22.3	70.40	3574.4	100.6	3579.4	3579.2
84.35	26.1	84.41	3623.5	148.7	3632.6	3632.5
95.30	29.2	95.55	3661.8	188.0	3675.0	3675.1
134.15	36.2	134.55	3804.6	330.8	3841.3	3840.3

These results may be expressed by the formula—

$$3336.738 + 3.268\,830t + 0.001\,553\,32t^2 + 0.000\,014\,664t^3,$$

which affords the numbers seen in the last columns of the above tables.

Dividing through by the first term, and correcting for the expansion of the glass (0.00002553), this formula becomes—

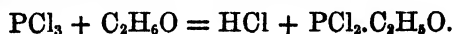
$$V = 1 + 0.001\,005\,18t + 0.000\,000\,490\,530t^2 + 0.000\,000\,004\,406\,5t^3,$$

by the aid of which the following table showing the relative volume of phosphoryl bromochloride at every 5° between 0° and 140° is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	75	108001	573
5	100503	503	80	108581	580
10	101010	507	85	109169	588
15	101520	510	90	109765	596
20	102034	514	95	110370	605
25	102551	517	100	110983	613
30	103072	521	105	111606	623
35	103597	525	110	112238	632
40	104128	531	115	112879	641
45	104663	535	120	113530	651
50	105204	541	125	114191	661
55	105750	546	130	114864	673
60	106303	553	135	115548	684
65	106862	559	140	116243	695
70	107428	566	137.7	1.15894	—

Ethoxyphosphorus Chloride, $\text{PCl}_2\cdot\text{C}_2\text{H}_5\text{O}$.

155 grams of carefully dehydrated alcohol were added, drop by drop, with constant shaking, to 460 grams of phosphorus chloride; these proportions being demanded by the equation—



The flask containing the chloride was surrounded by cold water and connected with an upright condenser. The mixture was allowed to stand for some time, and then submitted to distillation, and all coming over between 95° and 125° was collected separately. On rectification a large quantity of liquid was readily obtained boiling constantly at 117° to 118°.

A determination of the amount of chlorine in the liquid showed that it was practically pure.

1.1200 gram gave 2.2078 grams of silver chloride.

	Found.	Calculated.
Cl	48.58	48.26

The fraction employed in the determination of the specific gravity and rate of expansion, boiled at 117.8° ; $t = 0$; $n = 0$. Bar. 768.5 mm. Corrected and reduced boiling point 117.5° .

Two determinations of specific gravity gave—

I	1.30526
II	1.30527

at 0° compared with water at 4° .

The following observations of the rate of thermal expansion were made in Dilatometer E.

In the water-bath :—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
10.32	2895.8	2896.0	51.61	3028.8	3028.9
19.59	2924.7	2924.5	59.16	3054.6	3055.0
29.68	2956.5	2956.5	68.99	3089.8	3089.6
39.67	2989.0	2988.9	80.25	3130.6	3130.8

In the oil-bath :—

T° .	t° .	T^{Δ} .	V.	E.	Observed.	Calculated.
89.71	26.9	89.85	3152.3	179.1	3165.5	3166.0
97.72	30.3	97.99	3180.9	207.6	3197.6	3197.5
103.87	31.6	104.26	3202.2	229.0	3222.3	3221.9

These results lead to the formula—

$$2865.959 + 2.89462t + 0.00529388t^2 - 0.000002982t^3,$$

which affords the numbers seen in the last columns of the above tables.

Dividing through by the first term, and correcting for the expansion of the glass (0.00002303), this formula becomes—

$$V = 1 + 0.00102304t + 0.00000187367t^2 - 0.0000000061t^3,$$

by the aid of which the following table, showing the relative volume of ethoxyphosphorus chloride at every 5° between 0° and 120° , is calculated :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	65	107425	625
5	100516	516	70	108058	633
10	101042	526	75	108701	643
15	101577	535	80	109352	651
20	102121	544	85	110012	660
25	102674	553	90	110681	669
30	103237	563	95	111358	677
35	103808	571	100	112043	685
40	104388	580	105	112737	694
45	104978	590	110	113439	703
50	105576	598	115	114150	711
55	106183	607	120	114869	719
60	106800	617	117·5	1·145087	—

Phosphenyl Chloride, $C_6H_5.PCl_2$.

I am indebted to Professor Michaelis, of Carlsruhe, the discoverer of phosphenyl chloride, for an extremely liberal supply of this remarkable and interesting compound. When received it was perfectly clear and transparent, but in course of time it had deposited a slight precipitate of free phosphorus.

Before distilling it was heated for some hours to $180-190^\circ$ in a sealed tube. It boiled very constantly between $218\cdot5^\circ$ and $219\cdot1^\circ$, the greater portion coming over at about $218\cdot7^\circ$; $t = 20^\circ$; $n = 191$. Bar. $763\cdot6$ mm. Corrected and reduced boiling point $224\cdot6^\circ$.

Its specific gravity was found to be $1\cdot3428$ at 0° compared with water at 4° .

Michaelis found the boiling point of phosphenyl chloride to be 222° , and its specific gravity $1\cdot319$ at 20° .

The following observations of its rate of expansion by heat were made in Dilatometer D.

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
11·94	3261·2	3261·1	63·50	3399·6	3399·1
22·58	3289·1	3289·0	79·58	3444·2	3444·1
31·72	3318·0	3318·2	99·65	3502·6	3502·2
48·36	3358·4	3357·7			

In the oil-bath:—

T°.	t°.	TA.	V.	E.	Observed.	Calculated.
119·15	37·1	119·27	3551·6	167·6	3561·5	3561·5
131·17	39·1	131·48	3585·4	201·4	3600·0	3599·8
144·02	42·0	144·57	3622·4	238·4	3642·0	3642·2
In vapour of aniline		183·77	—	—	3778·8	3778·9

These numbers lead to the formula—

$$3230\cdot02 + 2\cdot598\ 6t + 0\cdot000\ 411\ 71t^2 + 0\cdot000\ 009\ 236\ 9t^3,$$

which affords the numbers given in the last columns of the above tables.

Dividing through by the first term and correcting for the expansion of the glass (0·0000213), this expression becomes—

$$V = 1 + 0\cdot000\ 825\ 8t + 0\cdot000\ 000\ 144\ 61t^2 + 0\cdot000\ 000\ 002\ 863t^3,$$

by the aid of which the following table, showing the relative volume of phosphenyl chloride at every 10° between 0° and 230°, is calculated :—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	130	111609	996
10	100828	828	140	112631	1022
20	101660	832	150	113679	1048
30	102498	838	160	114756	1077
40	103345	847	170	115863	1107
50	104201	856	180	117003	1140
60	105069	868	190	118176	1173
70	105950	881	200	119385	1209
80	106846	896	210	120632	1247
90	107758	912	220	121916	1284
100	108689	931	230	123242	1326
110	109640	951			
120	110613	973	224·6	1·22522	—

Vanadyl Trichloride, VOCl₃.

Vanadium pentoxide was reduced to the trioxide by ignition in a stream of dry hydrogen, and the trioxide was heated in dry chlorine. I am indebted to Dr. Roscoe for the pentoxide: it was a portion of the sample employed by him in the determination of the atomic weight of vanadium, and had been prepared with great care: it was beautifully crystallised, and of a magnificent ruby-red colour when seen by transmitted light. The vanadyl trichloride was heated in a current of dry carbon dioxide for some time in order to free it from dissolved chlorine, and distilled into the flask in which its boiling point was to be

determined. It began to boil at 127.05° , the column rapidly rose to 127.15° , at which point it remained constant. $n = 10$, $t = 30^{\circ}$. Bar. 764.5 mm. Corrected and reduced boiling point, 127.19° .

Three determinations of specific gravity at 0° compared with water at 4° gave—

I	1.86550
II	1.86568
III	1.86557
Mean	1.86558

Compared with water at 4° , the specific gravity is 1.86534.

Roscoe observed that vanadyl trichloride boils at 126.7° , and had the specific gravity—

1.841 at 14.5°	= 1.8655 at 0°
1.836 „ 17.5	= 1.8653 „
1.828 „ 24.0	= 1.8665 „

I controlled the indications of the dilatometer by determining the amount of expansion suffered by the vanadyl trichloride on being heated in the specific gravity bottle from 0° to near 100° , i.e., in the steam from boiling water. The details of the experiments are as follows:—

I. Weight of vanadyl trichloride at 10° *in vacuo* 7.15114 grams.

Ditto, after having been heated to 100.37° ,

bar. 770.3 mm. 6.66541 „

Expansion of glass for 1° 0.00002633

Hence 10,000 vols. at 0° become at 100.37° —

Observed 11090

Calculated 11091

II. Weight of vanadyl trichloride at 0° *in vacuo* 7.15156 grams.

Ditto, after having been heated to 100.10° ,

bar. 762.9 mm. 6.46736 „

Expansion of glass for 1° 0.00002633

Hence 10,000 vols. at 0° become at 100.10° —

Observed 11087

Calculated 11088

Observations of the rate of thermal expansion in Dilatometer C afforded the following results:—

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2968·7	2968·7	35·09	3070·5	3070·3
11·38	3000·6	3000·8	45·85	3103·2	3103·1
22·73	3033·8	3033·6	56·99	3137·7	3137·9

In the oil-bath :-

T° .	t° .	T^{Δ} .	V.	E.	Observed.	Calculated.
35·63	20·1	35·51	3070·7	44·0	3071·4	3071·5
46·73	21·7	46·71	3103·9	77·2	3105·8	3105·7
68·97	21·7	68·89	3169·7	143·0	3176·6	3176·4
80·16	24·1	80·32	3204·0	177·3	3214·3	3214·2
91·55	27·0	91·79	3239·5	212·7	3253·9	3254·1
102·92	29·4	103·40	3275·8	249·1	3295·6	3295·6
114·72	34·7	114·84	3312·3	285·6	3337·3	3337·8
124·81	37·2	125·06	3346·2	319·4	3377·4	3376·9

These numbers afford the formula

$$2968.679 + 2.792 15t + 0.002 597 68t^2 + 0.000 009 410 76t^3,$$

which on dividing through by the first term and correcting for the expansion of the glass (0.0000247) becomes—

$$V = 1 + 0.000 965 236t + 0.000 000 898 260t^2 + 0.000 000 003 191 63t^3.$$

By the aid of this formula the following table has been calculated : it shows the relative volumes of vanadyl trichloride at every 5^{Δ} between 0^{Δ} and its boiling point.

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107306	565
5	100485	485	75	107879	573
10	100975	490	80	108460	581
15	101469	494	85	109050	590
20	101969	500	90	109647	597
25	102474	505	95	110254	607
30	102985	511	100	110870	616
35	103502	517	105	111495	625
40	104025	523	110	112129	634
45	104555	530	115	112774	645
50	105091	536	120	113428	654
55	105634	543	125	114092	664
60	106184	550	130	114767	675
65	106741	557	127·19	1.143867	—

Arsenic Trifluoride, AsF₃.

Obtained by heating an intimate mixture of fluorspar and arsenious oxide with fuming oil of vitriol. An ordinary retort may be employed in the preparation, as the dry hydrofluoric acid simultaneously evolved has very little action on the glass. Large quantities of the fluoride may be readily prepared in this way, as much as 500 grams having been obtained in a single operation. On distillation the greater part of the liquid was found to boil constantly between 60·1° and 60·3°. $n = 0$, $t = 0$. Bar. 763·0 mm. Corrected and reduced boiling point, 60·4°.

In order to analyse it, a weighed portion of the fluoride was decomposed by water in a platinum dish, and after the addition of a few drops of hydrochloric acid, the arsenic was precipitated as sulphide.

0·4740 gram of fluoride gave 0·4415 gram of arsenic sulphide.

	Found.	Calculated.
Arsenic	56·85	56·91

Arsenic trifluoride is a heavy oily liquid, extremely volatile and readily decomposed by water with the formation of hydrochloric and arsenious acids. An admixture of a small quantity of water produces no turbidity: on adding excess, arsenious oxide gradually separates out in octohedra. Absolute alcohol and ether are miscible with the fluoride; chloroform is dissolved by it when hot, but separates out again on cooling. As arsenic trifluoride acts slowly upon glass, especially on flint glass, with the formation of silicon tetrafluoride, I determined its specific gravity and rate of expansion in a special apparatus, as I was unwilling to risk its action upon my dilatometers and specific gravity flasks.

Determination of specific gravity:—

Weight of bottle + AsF ₃ at 12·6° <i>in vacuo.</i>	21·6417	grams.
“ “ + water.....	10·7765	“
“ (empty).....	4·0720	“

From these numbers we obtain 2·6206 as the sp. gr. of arsenic fluoride at 12·6 compared with water at the same temperature; at 0° compared with water at 4° it is 2·6659.

The rate of expansion was determined by ascertaining the weight of the fluoride required to fill the specific gravity bottle at various temperatures. The results must be considered as only approximate, as the glass was found to be slowly acted upon in the course of the observations, more particularly at the higher temperatures. The bottle was weighed from time to time during the observations, and

the results corrected for the slight loss of weight suffered by the glass.

Temp.	Observed.	Calculated.	Temp.	Observed.	Calculated.
0·0°	10000	10000	36·2°	10516	10517
5·8	10079	10082	42·2	10604	10603
12·5	10187	10178	49·7	10706	10711
20·0	10277	10284	59·8	10861	10859
28·7	10407	10409			

These results may be expressed with sufficient accuracy by the formula—

$$V = 1 + 0\cdot001\,418t + 0\cdot000\,000\,262t^2,$$

by means of which the numbers in the third column are calculated.

Assuming $0\cdot000025$ as the expansion-coefficient of the glass (soda-lime glass of German make), the above formula becomes—

$$V = 1 + 0\cdot001\,443t + 0\cdot000\,000\,297t^2,$$

by means of which the following table, showing the relative volumes of arsenic trifluoride at every 5° between 0° and 65° , is calculated. It will be seen that the rate of expansion although rapid is very uniform :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	10000	—	35	10509	73
5	10072	72	40	10582	73
10	10145	73	45	10655	73
15	10217	72	50	10729	74
20	10290	73	55	10803	74
25	10363	73	60	10876	73
30	10436	73	65	10951	75

Arsenic Trichloride, AsCl₃.

Prepared by heating arsenic trioxide in a stream of dry chlorine. The product was distilled upwards for some time in a current of dry carbon dioxide in order to remove dissolved chlorine. Care is necessary to exclude moisture, as the least trace of water renders the liquid turbid, owing to the formation of the oxychloride, $\text{As}(\text{OH})_2\text{Cl}$.

On distillation the whole of the liquid was found to boil between $129\cdot23^\circ$ and $129\cdot33^\circ$, the greater portion coming over at $129\cdot30^\circ$. $n = 16$, $t = 15\cdot5$. Bar. $733\cdot4$ mm. Corrected and reduced boiling point $130\cdot21^\circ$.

The specific gravity of the chloride was found to be 2·15761 at 8·08°, compared with water at the same temperature. At 0° it is 2·20500 compared with water at 4°: this number is almost identical with that found by Pierre, viz., 2·20495. According to Haagen, arsenic trichloride boils at 128° under a pressure of 754 mm., and has a specific gravity of 2·1668 at 20°: this reduced to 0° is 2·2067.

Observations of the rate of expansion made with Dilatometer C gave in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2949·6	2949·7	23·34	3017·8	3017·7
8·01	2972·7	2972·7	35·31	3053·9	3053·8
11·62	2983·2	2983·2	47·10	3090·3	3090·2

In the oil-bath:—

T°.	t°.	TΔ.	V.	E.	Observed.	Calculated.
59·67	15·9	59·53	3123·5	136·8	3129·6	3129·8
70·35	12·9	70·33	3155·1	168·4	3165·2	3165·1
82·75	17·1	82·92	3193·0	206·4	3207·4	3207·4
94·26	22·7	94·61	3229·3	242·6	3248·0	3248·1
106·30	25·3	106·93	3266·9	280·3	3291·9	3292·3
117·50	26·2	117·69	3300·6	313·9	3332·4	3332·1
128·93	30·9	129·29	3338·3	348·6	3376·9	3376·5

These observations lead to the formula—

$$2949·690 + 2·851\ 284t + 0·002\ 434\ 26t^2 + 0·000\ 008\ 066\ 5t^3,$$

On dividing through by the first term and correcting for the expansion of the glass (0·0000247) this becomes—

$$V = 1 + 0·000\ 991\ 338t + 0·000\ 000\ 849\ 14t^2 + 0·000\ 000\ 002\ 755\ 1t^3,$$

by means of which the following table, showing the relative volume of arsenic trichloride at every 5° between 0° and its boiling point, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107449	571
5	100498	498	75	108028	579
10	101000	502	80	108615	587
15	101507	507	85	109209	594
20	102019	512	90	109811	602
25	102536	517	95	110420	609
30	103058	522	100	111038	618
35	103586	528	105	111664	626
40	104119	533	110	112299	635
45	104658	539	115	112942	643
50	105203	545	120	113595	653
55	105755	552	125	114257	662
60	106313	558	130	114929	672
65	106878	565	130.21	1.14956	—

The thermal expansion of arsenic trichloride may be represented according to Pierre by the formula—

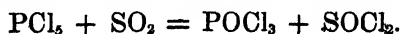
$$V = 1 + 0.000\,979\,072\,746t + 0.000\,000\,966\,948\,200t^2 + 0.000\,000\,001\,777\,204t^3,$$

which gives results uniformly lower than that afforded by my observations—

	30°.	60°.	90°.	120°.
Pierre	1.03029	1.06261	1.09724	1.13448
Thorpe.	1.03040	1.06295	1.09805	1.13602

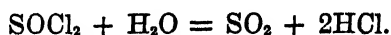
Thionyl Chloride, SOCl₂.

This substance is readily obtained by the action of sulphur dioxide upon phosphorus pentachloride. About 400 grams of the pentachloride were treated in successive portions of 100 grams with sulphur dioxide. The reaction begins even in the cold, and sufficient heat is generated during the process to bring about the speedy transformation of the materials into phosphoryl and thionyl chlorides :



By repeated fractionation the thionyl chloride was obtained boiling constantly between 77.2° and 78.2°, the greater portion of the liquid appearing to come over between 77.6° and 77.9°. $n = 18$, $t = 20$. Bar. 738.6 mm. Corrected and reduced boiling point, 78.8°.

Thionyl chloride when treated with water is decomposed in accordance with the equation—



Advantage was taken of this decomposition to determine the purity of the liquid by estimating the amount of sulphurous acid yielded by

a known weight of the substance. 0·3859 gram of the thionyl chloride was decomposed by water, the solution made up to about 600 c.c., and mixed with 50 c.c. of decinormal iodine solution (1 c.c. = 0·012685 gram iodine), next a few c.c. of starch-paste, and a further addition of the iodine solution until the blue colour was persistent. In all 65·90 c.c. of the iodine solution were needed.

SO calculated . . 40·4 per cent. Found . . 40·8 per cent.

Two determinations gave for the specific gravity at 0°, compared with water at 4°:—

I	1·67672
II	1·67674
Mean	1·67673

According to Wurtz, thionyl chloride boils at 78°, and has a specific gravity of 1·675 at 0°. These numbers agree closely with those resulting from my own experiments.

A series of observations of the rate of the thermal expansion of thionyl chloride made in Dilatometer N, in the water-bath, afforded the following numbers:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
15·64	3418·9	3419·1	44·54	3537·4	3537·2
19·64	3435·0	3434·9	49·27	3557·8	3557·6
23·57	3450·6	3450·6	53·93	3577·5	3577·9
28·90	3472·0	3472·1	58·93	3600·0	3599·6
33·70	3491·8	3491·7	64·59	3626·0	3626·0
39·30	3515·0	3515·0	68·75	3645·4	3645·3

These numbers lead to the formula—

$$3358·587 + 3·814\,281t + 0·002\,972\,69t^2 + 0·000\,031\,954t^3,$$

by means of which the volumes in the last column of the above table are calculated.

Dividing through by the first term and correcting for the expansion of the glass (0·00002553), we obtain:—

$$V = 1 + 0·001\,164\,19t + 0·000\,000\,914\,18t^2 + 0·000\,000\,009\,536\,8t^3,$$

by the aid of which the following table, showing the relative volume of thionyl chloride at every 5° between 0° and 80°, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	45	105511	647
5	100585	585	50	106169	658
10	101174	589	55	106838	669
15	101770	596	60	107520	682
20	102373	603	65	108215	695
25	102983	610	70	108924	709
30	103601	618	75	109648	724
35	104228	627	80	110387	739
40	104864	636	78·8	1·10208	—

Sulphothionyl Chloride, SSCl_2 .

About 500 grams of commercial sulphur chloride, which had been allowed to stand in contact with fragments of roll sulphur for some months, was distilled. It began to boil at about 135° , and a few drops of dark red liquid came over, after which the thermometer gradually rose to 139° , between which limits the whole of the chloride distilled. By repeated distillation, it was obtained of the constant boiling point $137\cdot62^\circ$; $n = 25$, $t = 18^\circ$. Bar. 761·2 mm. Corrected and reduced boiling point, $138\cdot12^\circ$.

A determination of specific gravity gave 1·69802 at $7\cdot58^\circ$, compared with water at the same temperature. At 0° , compared with water at 4° , this becomes 1·70941.

Other observations on record are:—

Dumas.....	138°	Bar ?	Sp. gr. 1·687	at ?
Marchand	139	„	1·686	„
Kopp	144	760 mm.	1·6802	„ $16\cdot7^\circ$
			1·7055	„ 0°
Haagen	$137\cdot7$	761·4 mm.	1·6828	„ 20°

The following observations of the rate of thermal expansion of this liquid were made in Dilatometer C:—

In the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	2965·0	2964·7	37·16	3066·9	3067·1
12·51	2998·5	2998·6	49·08	3101·6	3101·3
24·74	3032·1	3032·2	62·13	3139·4	3139·5

In the oil-bath:—

T°.	t°.	T ^Δ .	V.	E.	Observed.	Calculated.
62·36	19·1	62·24	3133·7	147·5	3139·7	3139·8
74·77	23·2	74·79	3168·7	182·5	3177·8	3177·8
86·87	26·3	87·04	3203·5	217·3	3216·4	3216·1
100·59	29·1	101·09	3243·0	256·8	3261·3	3261·5
112·36	22·9	112·52	3273·6	287·4	3300·7	3299·9
124·83	29·6	125·17	3311·7	325·5	3343·6	3343·9
136·40	33·5	136·94	3347·0	360·8	3386·0	3386·5

These numbers lead to the formula—

$$2964\cdot687 + 2\cdot696\ 519t + 0\cdot001\ 151\ 35t^2 + 0\cdot000\ 012\ 083\ 8t^3,$$

which, on dividing through by the first term and correcting for the expansion of the glass (0·00002470), becomes

$$V = 1 + 0\cdot000\ 934\ 25t + 0\cdot000\ 000\ 410\ 82t^2 + 0\cdot000\ 000\ 004\ 076\ 9t^3,$$

The following table is calculated by means of this formula; it shows the relative volume of sulphothionyl chloride at every 5^Δ between 0^Δ and 140^Δ :—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	75	107410	529
5	100468	468	80	107946	536
10	100939	471	85	108488	542
15	101412	473	90	109038	550
20	101888	476	95	109596	558
25	102368	480	100	110160	564
30	102851	483	105	110733	573
35	103338	487	110	111315	582
40	103829	491	115	111907	592
45	104324	495	120	112507	600
50	104825	501	125	113116	609
55	105329	504	130	113735	616
60	105841	512	135	114364	629
65	106358	517	140	115003	639
70	106881	523	188·12	1·14571	—

The rate of expansion of this liquid has already been observed by Kopp, who has expressed his results by the formula—

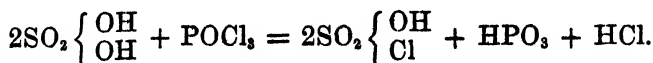
$$V = 1 + 0\cdot000\ 959\ 1t - 0\cdot000\ 000\ 0381\ 85t^2 + 0\cdot000\ 000\ 007\ 318\ 6t^3.$$

This expression represents a slightly quicker rate than would be indicated by my observations, as the following comparison shows :—

	30°.	60°.	90°.	120°.
Kopp	10290	10590	10913	11271
Thorpe	10284	10583	10903	11251

Chlorosulphonic Acid, SO₂.OHCl.

I prepared this compound by the action of phosphoryl chloride upon concentrated sulphuric acid.



226 grams of phosphoryl chloride were mixed with 200 grams of the strongest oil of vitriol, and the mixture was gently heated and afterwards distilled. The greater portion of the liquid boiled between 153° and 154°, and, on redistillation, very nearly the whole came over between 153·3° and 153·6°, $n = 61$, $t = 27^\circ$. Bar. 745·6 mm. Corrected and reduced boiling point, 155·3°.

The liquid was analysed by breaking a bulb containing a known quantity beneath the surface of water in a well-stoppered bottle, and determining the amount of soda needed for complete neutralisation.

Chlorosulphonic acid taken	0·9628	gram.
Caustic soda (NaHO) needed	0·9958	„
„ „ „ calculated	0·9917	„

Two determinations of specific gravity at 0°, compared with water at 4°, gave:—

I	1·78465
II	1·78483
Mean	1·78474

According to Michaelis, chlorosulphonic acid boils at 158·4°, and has a specific gravity of 1·776 at 18°.

The following observations of its rate of expansion by heat were made in Dilatometer N in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
10·98	3377·2	3377·7	64·42	3538·3	3538·5
25·34	3420·8	3420·5	73·90	3567·5	3567·9
36·64	3454·4	3454·2	89·05	3615·6	3615·7
48·61	3489·6	3489·9	100·05	3650·7	3651·1

These numbers afford the formula—

$3345·551 + 2·942\ 465t + 0·000\ 321\ 819t^2 + 0·000\ 008\ 001\ 76t^3$,
which, on dividing through by the first term and correcting for the expansion of the glass (0·00002553), becomes—

$$V = 1 + 0·000\ 905\ 05t + 0·000\ 000\ 118\ 647t^2 + 0·000\ 000\ 002\ 394\ 3t^3.$$

Assuming that this formula may be taken to represent the expansion of chlorosulphonic acid from 0° to its boiling point, the following table gives the relative volumes at every 5° between 0° and 160°:—

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	85	107926	487
5	100453	453	90	108416	480
10	100906	453	95	108910	494
15	101361	455	100	109409	499
20	101817	456	105	109911	502
25	102274	457	110	110418	507
30	102732	458	115	110929	511
35	103193	461	120	111445	516
40	103655	462	125	111966	521
45	104118	463	130	112492	526
50	104585	467	135	113024	532
55	105053	468	140	113560	536
60	105525	472	145	114103	543
65	105999	474	150	114651	548
70	106476	477	155	115205	554
75	106956	480	160	115765	560
80	107439	483	155·3	1·15238	—

Sulphuryl dichloride, SO₂Cl₂.

This substance was prepared by the very convenient method of Behrend, based on the decomposition of chlorosulphonic acid at a high temperature. When heated to about 200° for some hours, chlorosulphonic acid is almost completely resolved into sulphuryl dichloride and sulphuric acid; thus:—



The sulphuryl chloride is readily separated from the oil of vitriol by distillation. The product obtained from about 170 grams of the chlorosulphonic acid boiled with remarkable constancy at 69·1°, $n = 40$, $t = 25$. Bar. 750·5 mm. Corrected and reduced boiling point, 69·95°.

Two estimations of the specific gravity at 0°, compared with water at 4°, gave:—

I	1·70816
II	1·70812
Mean	1·70814

The following observations of the thermal expansion of this compound were made in Dilatometer E in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
15.63	2909.9	2909.9	44.54	3017.0	3016.8
19.64	2924.3	2924.3	49.27	3035.6	3035.4
23.57	2938.4	2938.4	53.93	3053.8	3053.9
28.89	2957.8	2957.8	58.93	3074.3	3074.3
33.70	2975.8	2975.6	64.59	3098.0	3098.0
39.30	2996.7	2996.8	68.75	3115.9	3115.8

These numbers may be represented by the formula—

$$2855.411 + 3.448\,264t + 0.002\,088\,89t^2 + 0.000\,041\,505t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (0.00002303), becomes—

$$V = 1 + 0.001\,230\,65t + 0.000\,000\,759\,375t^2 + 0.000\,000\,014\,587t^3.$$

The following table, calculated by means of this formula, shows the relative volumes of sulphuryl dichloride at every 5° between 0° and 70° :—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	40	105138	675
5	100617	617	45	105825	687
10	101240	623	50	106526	701
15	101868	628	55	107241	715
20	102503	635	60	107973	732
25	103147	644	65	108720	747
30	103800	653	70	109487	767
35	104463	663	69.95	1.09479	—

Disulphuryl Chloride, S₂O₆Cl₂.

Made by the action of sulphur chloride upon sulphur trioxide. The product boiled almost completely between 135° and 138° , and on redistillation came over almost entirely between 138.3° and 138.4° , the greater portion collecting at 138.37° . $n = 48^\circ$, $t = 19.3$. Bar. 758.8 Corrected and reduced boiling point 139.59° .

The liquid was analysed by decomposing a known weight with water and determining the amount of sodium hydrate needed for neutralisation.

Weight of disulphuryl chloride taken 1.3636 grams.

„ sodium hydrate needed 1.5212 „

„ „ „ calculated 1.5220 „

Two determinations of specific gravity were made at 0° —

I	1·85824
II	1·85868
Mean	1·85846

compared with water at 4^Δ.

According to Michaelis this compound has a specific gravity of 1·819 at 18° and boils at 146°.

Observations of the rate of the thermal expansion of this liquid were made in Dilatometer E with the following results (the observations were made concurrently with those of chlorosulphonic acid):—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
10·93	2862·8	2863·0	64·42	3017·2	3017·3
25·34	2903·0	2902·9	73·90	3046·3	3046·5
36·64	2935·1	2935·1	89·05	3094·9	3094·6
48·51	2969·6	2969·6	100·05	3130·5	3130·6

These numbers afford the formula—

$$2833·444 + 2·678\ 383t + 0·002\ 395\ 19t^2 + 0·000\ 005\ 221\ 5t^3,$$

which gives results agreeing closely with those directly observed.

On dividing through by the first term and correcting for the expansion of the glass (0·00002303), this expression becomes—

$$V = 1 + 0·000\ 968\ 30t + 0·000\ 000\ 867\ 098t^2 + 0·000\ 000\ 018\ 623t^3.$$

By means of this formula the following table is calculated. It shows the relative volumes of disulphuryl chloride at every 5^Δ from 0^Δ to 140^Δ, on the assumption that the formula is valid between these limits.

Δ.	Volume.	Diff.	Δ.	Volume.	Diff.
0	100000	—	75	107829	562
5	100486	486	80	108397	568
10	100977	491	85	108971	574
15	101473	496	90	109553	582
20	101973	500	95	110141	588
25	102478	505	100	110736	595
30	102988	510	105	111339	603
35	103503	515	110	111948	609
40	104024	521	115	112565	617
45	104550	526	120	113190	625
50	105082	532	125	113822	632
55	105619	537	130	114463	641
60	106162	543	135	115111	648
65	106711	549	140	115767	656
70	107267	556	139·59	1·15713	—

Chromyl Dichloride, CrO₂Cl₂.

A large quantity of this liquid was prepared by the action of strong sulphuric acid upon a well-dried mixture of common salt and potassium dichromate. On distillation a perfectly clear product, free from the solid trichromyl dichloride, (CrO₂)₃Cl₂, was obtained; it boiled constantly at 115·77°. $n = 0^\circ$, $t = 0^\circ$. Bar. 757·7 mm. Corrected and reduced boiling point 115·9°.

Its specific gravity was found to be 1·93540 at 14·48° compared with water at the same temperature; at 0° compared with water at 4° it is 1·96101. In a former communication (*Chem. Soc. J.*, 1868) I have given the boiling point of chromyl dichloride as 116·8° and its specific gravity as 1·920 at 25° compared with water at the same temperature. This reduced to 0°, and compared with water at 4°, becomes 1·9617.

The following observations of the thermal expansion of chromyl dichloride were made in Dilatometer D in the water-bath:—

Δ .	Observed.	Calculated.	Δ .	Observed.	Calculated.
0·00	3322·6	3322·7	52·81	3497·4	3497·6
10·82	3356·9	3356·8	64·88	3541·2	3541·0
20·82	3389·1	3389·1	73·61	3573·4	3573·2
31·05	3422·9	3422·9	84·12	3612·8	3612·8
42·13	3460·5	3460·4	99·85	3674·3	3674·3

These results may be accurately represented by the formula—

$$3322\cdot658 + 3\cdot114\ 312t + 0\cdot003\ 501\ 27t^2 + 0\cdot000\ 005\ 812\ 7t^3,$$

which, on dividing through by the first term, and correcting for the expansion of the glass (0·0000213), becomes—

$$1 + 0\cdot000\ 958\ 60t + 0\cdot000\ 001\ 073\ 7t^2 + 0\cdot000\ 000\ 001\ 962t^3,$$

by means of which the following table, showing the relative volumes of chromyl dichloride at every 5° between 0° and its boiling point, is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	70	107304	565
5	100482	482	75	107877	573
10	100969	487	80	108457	580
15	101463	494	85	109044	587
20	101962	499	90	109640	596
25	102466	504	95	110244	604
30	102978	512	100	110856	612
35	103495	517	105	111476	620
40	104019	524	110	112105	629
45	104549	530	115	112741	636
50	105086	537	120	113388	647
55	105630	544			
60	106181	551	115.9	1.12856	—
65	106739	558			

Carbon Bisulphide, CS₂.

The thermal expansion of [this liquid has already been studied by Muncke (*Ann. Chim. Phys.* [2], **64**, 5, 1837), Pierre, and Hirn, but their observations were necessarily made upon imperfectly purified material, as the method of obtaining carbon bisulphide free from the sulphuretted products which give it the extremely disagreeable smell which it ordinarily possesses, has only been discovered within the last few years. Although the amount of the foreign substances present in the particular specimens with which the observations above referred to were made was probably very small—too small, it may be, to materially affect the rate of expansion—it seemed advisable to repeat the determinations upon the properly purified liquid, on account of the special interest which attaches to a knowledge of the specific volume of this liquid.

About 500 grams of carefully rectified carbon bisulphide were digested with a large quantity of corrosive sublimate for 10 or 12 weeks. The liquid was next agitated with metallic mercury, distilled off white wax, digested with phosphoric pentoxide, and again distilled, care being taken to protect the liquid throughout the whole series of operations as much as possible from light (compare Herwig, *Pogg. Ann.*, **137**, 19 and 592). The bisulphide thus obtained was perfectly colourless, and possessed a faint aromatic odour, recalling that of chloroform. It boiled absolutely constantly at 45.95° , $n = 49^{\circ}$, $t = 17.0^{\circ}$. Bar., 767.2. Corrected and reduced boiling point, 46.04° .

Two determinations of specific gravity at 0° compared with water at 0° , gave—

I	1.29233
II	1.29232

Compared with water at 4°, the specific gravity is 1·29215.

Other observations on record are—

Gay-Lussac....	46·6	at 760 mm.	Sp. gr ..	1·2905	at 0°.
Regnault.....	46·20	„ 760 „			
Pierre.....	47·9	„ 755·8 mm.		1·2931	„ 0°.
Andrews.....	46·2	„ 769 „			
Buff.....	46·0	„ 760 „		1·30534 and 1·29182	at 0°.

Two series of observations of the expansion were made. With Dilatometer B in the water-bath:—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	2890·6	2890·3	24·23	2971·7	2971·6
4·08	2903·6	2903·6	27·81	2984·4	2984·2
8·01	2916·6	2916·6	31·87	2998·7	2998·7
11·89	2929·5	2929·5	35·99	3013·9	3013·7
15·82	2942·6	2942·7	39·84	3027·9	3027·9
19·74	2956·5	2956·1	44·81	3046·9	3046·7

These numbers lead to the formula—

$$2890·300 + 3·252\ 82t + 0·003\ 125\ 97t^2 + 0·000\ 048\ 714t^3.$$

The second series made in Dilatometer C gave—

Δ.	Observed.	Calculated.	Δ.	Observed.	Calculated.
0·00	3001·6	3001·4	24·23	3086·1	3086·0
4·08	3015·3	3015·3	27·81	3099·2	3099·1
8·01	3028·7	3028·7	31·87	3114·3	3114·2
11·89	3042·2	3042·1	35·99	3130·2	3129·8
15·82	3055·9	3055·9	39·84	3144·7	3144·6
19·74	3070·1	3069·8	44·81	3164·1	3164·3

numbers which afford the formula—

$$3001·420 + 3·378\ 051t + 0·003\ 285\ 74t^2 + 0·000\ 054\ 151t^3.$$

On dividing through by the first terms and correcting for the expansion of the glass, these formulæ became respectively—

$$(I.)\ 1 + 0·001\ 150\ 93t + 0·000\ 001\ 109\ 89t^2 + 0·000\ 000\ 016\ 882t^3.$$

and

$$(II.)\ 1 + 0·001\ 150\ 19t + 0·000\ 001\ 122\ 53t^2 + 0·000\ 000\ 018\ 069t^3.$$

The mean formula is—

$$(III)\ V = 1 + 0·001\ 150\ 56t + 0·000\ 001\ 116\ 21t^2 + \\ \dots\dots\dots 0·000\ 000\ 017\ 475\ 5t^3,$$

by the aid of which the following table, showing the relative volume of carbon bisulphide at every 5° between 0° and 50° , is calculated:—

Δ .	Volume.	Diff.	Δ .	Volume.	Diff.
0	100000	—	30	103599	626
5	100578	578	35	104238	639
10	101163	585	40	104892	654
15	101757	594	45	105563	671
20	102360	603	50	106250	687
25	102973	613	46·04	1·05704	—

The observations already referred to have yielded the following formulæ:—

$$\text{Muncke} \dots\dots 1 + 0\cdot001\,125\,691t + 0\cdot000\,001\,715\,049t^2 + 0\cdot000\,000\,001\,211\,66t^3$$

$$\text{Pierre} \dots\dots 1 + 0\cdot001\,139\,8t + 0\cdot000\,001\,370\,7t^2 + 0\cdot000\,000\,019\,123t^3$$

$$\text{Hirn} \dots\dots 1 + 0\cdot001\,168\,06t + 0\cdot000\,001\,649\,0t^2 - 0\cdot000\,000\,000\,811\,19t^3 + 0\cdot000\,000\,000\,060\,95t^4 \quad (30^{\circ} \text{ to } 160^{\circ})$$

My own results agree most closely with those of Pierre. Hirn's formula is, strictly speaking, only applicable to temperatures above the boiling point of carbon bisulphide. Muncke's observations are unquestionably too low.

	15° .	30° .	45° .
Muncke	101728	103535	105424
Hirn.....	101789	103650	105583
Pierre	101747	103594	105581
Thorpe.....	101744	103576	105536

III. DISCUSSION OF ERRORS.

The foregoing pages contain the results of observations made upon 47 liquids. Before proceeding to indicate and discuss the conclusions to which the investigation leads it may be desirable to collect together in synoptical form the numerical data upon which a discussion must depend. These data are embodied in the following tables.

Table I gives the several values of the coefficients in the expression—

$$V = 1 + at + bt^2 + ct^3,$$

representing the thermal expansions of the particular liquids investigated.

TABLE I.

Substance.	a.	b.	c.
Bromine	0·001 062 18	0·000 001 877 14	-0·000 000 003 085
Iodine monochloride..	0·000 915 90	0·000 000 832 96	0·000 000 002 750
Ethylene bromide	0·000 952 85	0·000 000 683 46	0·000 000 003 947
Ethylene chloriodide..	0·000 936 92	0·000 000 415 13	0·000 000 004 501
Ethylene chloride	0·001 153 03	0·000 000 825 69	0·000 000 009 625
Ethidene chloride	0·001 284 02	0·000 001 890 62	0·000 000 007 848
Acetyl chloride	0·001 369 48	0·000 002 073 90	0·000 000 012 185
Trichloroacetyl chloride	0·001 091 13	0·000 000 272 05	0·000 000 008 293
Chloral	0·001 087 15	0·000 002 803 06	-0·000 000 016 040
Pentachlorethane	0·000 949 01	-0·000 000 074 50	0·000 000 005 280
Methene chloride	0·001 308 05	0·000 002 735 00	-0·000 000 001 330
Chloroform	0·001 230 24	0·000 001 713 80	0·000 000 008 338
Chloropicrin	0·001 100 70	0·000 000 465 76	0·000 000 007 833
Carbon tetrachloride..	0·001 207 19	0·000 000 671 09	0·000 000 013 478
Bromoform.....	0·000 941 16	0·000 000 278 00	0·000 000 004 260
Trichlorobromomethane	0·001 082 31	0·000 000 655 82	0·000 000 005 858
Propionitrile	0·001 227 75	0·000 002 040 64	0·000 000 004 675
Epichlorhydrin	0·001 026 60	0·000 000 619 74	0·000 000 006 657
Allyl alcohol	0·000 993 71	0·000 000 599 86	0·000 000 012 285
Acetone	0·001 352 93	0·000 003 024 26	-0·000 000 000 290
Heptane	0·001 210 23	0·000 001 113 30	0·000 000 011 740
Ethyl-amy!	0·001 239 40	0·000 001 193 18	0·000 000 013 060
Octane.....	0·001 183 04	0·000 000 186 65	0·000 000 012 947
Di-isobutyl.....	0·001 197 01	0·000 000 621 22	0·000 000 014 166
Aniline	0·000 862 95	0·000 000 273 51	0·000 000 003 466
Picoline	0·000 966 53	0·000 000 845 90	0·000 000 004 567
Nitrogen tetroxide....	0·001 591	-0·000 003 970 15	0·000 000 215 3
Silicon tetrachloride ..	0·001 330 95	0·000 002 809 78	0·000 000 002 157
Titanium tetrachloride	0·000 982 61	0·000 000 505 53	0·000 000 005 131
Tin tetrachloride	0·001 160 55	0·000 000 646 17	0·000 000 007 727
Phosphorus trichloride	0·001 159 20	0·000 001 163 70	0·000 000 008 029
Phosphorus tribromide	0·000 841 17	0·000 000 542 89	0·000 000 001 889
Phosphoryl chloride ..	0·001 075 10	0·000 000 991 31	0·000 000 005 757
Thiophosphoryl chloro- ride	0·001 008 50	0·000 000 655 82	0·000 000 004 746
Phosphoryl bromo- chloride	0·001 005 20	0·000 000 490 53	0·000 000 004 407
Ethoxyphosphorus chloride	0·001 023 04	0·000 001 873 67	-0·000 000 000 610
Phosphenyl chloride ..	0·000 825 82	0·000 000 144 61	0·000 000 002 863
Vanadyl trichloride ..	0·000 965 24	0·000 000 898 26	0·000 000 003 192
Arsenic trifluoride....	0·001 443	0·000 000 297	—
Arsenic trichloride ..	0·000 991 84	0·000 000 849 14	0·000 000 002 755
Thionyl dichloride....	0·001 164 19	0·000 000 914 18	0·000 000 009 537
Sulphothionyl chloride	0·000 934 25	0·000 000 410 82	0·000 000 004 077
Chlorosulphonic acid..	0·000 905 05	0·000 000 118 65	0·000 000 002 394
Sulphuryl dichloride..	0·001 230 65	0·000 000 759 38	0·000 000 014 587
Disulphuryl chloride..	0·000 968 30	0·000 000 867 10	0·000 000 001 862
Chromyl dichloride ..	0·000 958 60	0·000 000 107 37	0·000 000 001 962
Carbon disulphide....	0·001 150 56	0·000 001 116 21	0·000 000 017 476

Table II shows the relative volumes of the several liquids at every 10° between 0° and their boiling points.

TABLE II.

$\Delta C.$	Bromine, Br.	Iodine monochloride, ICl.	Ethylene bromide, $C_2H_4Br_2$.	Ethylene chlor- iodide, C_2H_4ICl .	Ethylene chloride, $C_2H_4Cl_2$.	Ethylene chloride, $C_2H_4Cl_2$.	Acetyl chloride, C_2H_3OCl .	Trichloroacetyl chlo- ride, C_2OCl_4 .
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101081	100925	100960	100942	101162	101304	101391	101095
20	102197	101867	101936	101894	102347	102650	102832	102200
30	103347	102830	102931	102860	103559	104044	104328	103320
40	104592	103815	103946	103843	104806	105489	105888	104461
50	105742	104822	104984	104845	106092	106991	107518	105627
60	106983	105855	106049	105868	107423	108554	—	106824
70	—	106914	107140	106916	108806	—	—	108056
80	—	108001	108262	107992	110246	—	—	109328
90	—	109118	109417	109097	—	—	—	110645
100	—	110267	110607	110234	—	—	—	112013
110	—	—	111834	111408	—	—	—	113436
120	—	—	113101	112619	—	—	—	114918
130	—	—	114409	113871	—	—	—	—
140	—	—	—	115166	—	—	—	—

$\Delta C.$	Chloral, C_2Cl_3OH .	Pentachlorethane, C_2HCl_5 .	Methene chloride, CH_2Cl_2 .	Chloroform, $CHCl_3$.	Chloropicrin, $C(NO_2)_3$.	Carbon tetrachloride, CCl_4 .	Bromoform, $CHBr_3$.	Trichlorobromethane, CCl_3Br .
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101114	100949	101335	101248	101106	101215	100944	101089
20	102274	101899	102724	102536	102226	102452	101897	102196
30	103470	102855	104167	103867	103365	103718	102868	103322
40	104694	103818	105662	105248	104528	105022	103887	104472
50	105936	104792	—	106684	105718	106372	104829	105649
60	107186	105781	—	108179	106941	107776	105839	106857
70	—	106788	—	—	108202	109241	106870	108098
80	—	107815	—	—	109505	110777	107925	109378
90	—	108866	—	—	110855	—	109006	110699
100	—	109944	—	—	112256	—	110116	112065
110	—	111052	—	—	113714	—	111256	—
120	—	112193	—	—	—	—	112430	—
130	—	113371	—	—	—	—	113641	—
140	—	114587	—	—	—	—	114890	—
150	—	115349	—	—	—	—	116180	—
160	—	117156	—	—	—	—	—	—

TABLE II (continued).

$\Delta C.$	Propionitrile, $C_3H_5CN.$	Epichlorhydrin, $C_3H_5OCl.$	Allyl alcohol, $C_3H_5OH.$	Acetone, $C_3H_6O.$	Heptane, $C_7H_{16}.$	Ethyl-amyl, $C_7H_{16}.$	Octane, $C_8H_{18}.$	Di-isobutyl, $C_8H_{18}.$
0	100000	100000	100000	100000	100000	100000	100000	100000
10	101249	101033	101026	101383	101222	101253	101186	101205
20	102541	102083	102072	102827	102474	102537	102384	102430
30	103879	103154	103145	104330	103763	103861	103601	103685
40	105267	104248	104252	105894	105094	105232	104845	104978
50	106707	105371	105402	107517	106476	106659	106124	106317
60	108202	106526	106601	109200	107916	108148	107445	107712
70	109755	107718	107857	—	109420	109709	108817	109169
80	111367	108950	109176	—	110995	111348	110247	110699
90	113044	110227	110568	—	112650	113070	111742	112309
100	114786	111551	112038	—	114390	—	113312	114008
110	—	112929	—	—	—	—	114963	115804
120	—	114362	—	—	—	—	116702	—

$\Delta C.$	Aniline, $C_6H_7N.$	Picoline, $C_6H_7N.$	Nitrogen tetroxide, $N_2O_4.$	Silicon tetrachlo- ride, $SiCl_4.$	Titanium tetrachlo- ride, $TiCl_4.$	Tin tetrachloride, $SnCl_4.$	Phosphorus trichlo- ride, $PCl_3.$	Phosphorus tribro- mide, $PBr_3.$
0	100000	100000	100000	100000	100000	100000	100000	100000
10	100866	100975	101573	101359	100988	101168	101172	100847
20	101740	101971	103196	102776	101990	102353	102371	101706
30	102623	102988	—	104252	103007	103561	103604	102577
40	103518	104031	—	105787	104044	104795	104874	103463
50	104426	105101	—	107384	105104	106061	106187	104365
60	105351	106202	—	109044	106188	107363	107547	105283
70	106294	107337	—	—	107302	108706	108960	106218
80	107256	108507	—	—	108447	110094	110429	107173
90	108241	109717	—	—	109627	111532	—	108148
100	109250	110968	—	—	110845	113024	—	109143
110	110285	112263	—	—	112103	114576	—	110161
120	111348	113606	—	—	113406	—	—	111202
130	112442	114998	—	—	114756	—	—	112266
140	113569	—	—	—	116155	—	—	113357
150	114729	—	—	—	—	—	—	114476
160	115927	—	—	—	—	—	—	115622
170	117163	—	—	—	—	—	—	116796
180	118441	—	—	—	—	—	—	—

TABLE II (*continued*).

$\Delta C.$	Phosphoryl chloride, $POCl_3$.	Thiophosphoryl chloride, $PSCl_3$.	Phosphoryl bromide, $POBrCl_2$.	Ethoxyphosphorus chloride, $PCl_2 \cdot C_2H_5O$.	Phenyl chloride, $PCl_2 \cdot C_6H_5$.	Vanadyl chloride, $VOCl_3$.	Arsenic fluoride, AsF_3 .	Arsenic chloride, $AsCl_3$.
0	100000	100000	100000	100000	100000	100000	10000	100000
10	101086	101025	101010	101042	100828	100975	10145	101000
20	102194	102047	102034	102121	101660	101969	10290	102019
30	103330	103097	103072	103237	102498	102985	10436	103058
40	104496	104169	104128	104388	103345	104025	10582	104119
50	105696	105266	105204	105576	104201	105091	10729	105203
60	106932	106390	106303	106800	105069	106184	10876	106318
70	108209	107544	107428	108058	105950	107306	—	107449
80	109530	108781	108581	109352	106846	108460	—	108615
90	110898	109953	109765	110681	107758	109647	—	109811
100	112318	111215	110983	112043	108689	110870	—	111038
110	113792	112519	112238	113439	109640	112129	—	112299
120	—	113866	113530	114869	110613	113428	—	113595
130	—	—	114864	—	111609	114767	—	114929
140	—	—	116243	—	112631	—	—	—
150	—	—	—	—	113679	—	—	—
160	—	—	—	—	114756	—	—	—
170	—	—	—	—	115863	—	—	—
180	—	—	—	—	117003	—	—	—
190	—	—	—	—	118176	—	—	—
200	—	—	—	—	119385	—	—	—
210	—	—	—	—	120632	—	—	—
220	—	—	—	—	121916	—	—	—
230	—	—	—	—	123242	—	—	—

TABLE II (*continued*).

°C.	Thionyl chloride, SOCl ₂ .	Sulphothionyl chlo- ride, SSOCl ₂ .	Chlorosulphonic acid, SO ₂ HCl.	Sulphuryl dichlo- ride, SO ₂ Cl ₂ .	Disulphuryl chlo- ride, S ₂ O ₅ Cl ₂ .	Chromyl dichloride, CrO ₂ Cl ₂ .	Carbon bisulphide, CS ₂ .
0	100000	100000	100000	100000	100000	100000	100000
10	101174	100939	100906	101240	100977	100969	101163
20	102373	101888	101817	102503	101973	101962	102360
30	103601	102851	102732	103800	102988	102978	103599
40	104864	103829	103655	105138	104024	104019	104892
50	106169	104825	104585	106526	105082	105086	106250
60	107520	105841	105525	107973	106162	106181	—
70	108924	106881	106476	109487	107267	107304	—
80	110387	107946	107439	—	108397	108457	—
90	—	109038	108416	—	109553	109640	—
100	—	110160	109409	—	110736	110856	—
110	—	111315	110418	—	111948	112105	—
120	—	112507	111445	—	113190	113388	—
130	—	113735	112492	—	114463	—	—
140	—	115003	113560	—	115767	—	—
150	—	—	114651	—	—	—	—
160	—	—	115765	—	—	—	—

Table III shows the formulæ and molecular weights of these bodies, their boiling points under the standard pressure, their relative volumes at this temperature (vol. at 0° = 1), their specific gravities at 0° and at their respective boiling points, and lastly their specific volumes.

As the numerical value denoting the specific volume of a liquid depends upon the knowledge of its molecular weight and of its specific gravity at its boiling point under the standard pressure, or, what comes to the same thing, of its rate of thermal expansion, its point of ebullition, and its specific gravity at some other temperature, it is evident that this value, being founded on so wide an experimental basis, is liable to be affected with observational errors. It is desirable, therefore, in the outset, to trace the probable magnitude of these, and to indicate their effect upon the results, before we proceed to discuss their bearing on this question of the connection between the molecular weight of a body and its specific gravity when liquid.

1. *Errors of Atomic Weight.*—Of the 17 elementary bodies which enter into the composition of the material experimented upon in this investigation, the atomic weights of oxygen, chlorine, bromine, iodine, sulphur, nitrogen, and carbon are known with a very high degree of accuracy, certainly to within 0.05 of a unit. The atomic

TABLE III.

Substance.	Formula.	Mol. weight.	B. p. °A.	Vol. at b. p.	Sp. gr. at 0°.	Sp. gr. at b. p.	Sp. vol.
Bromine	Br ₂	159.50	59.27	1.06911	3.18828	2.98218	53.48
Iodine monochloride	ICl	161.90	101.3	1.10419	3.18223	2.88196	56.18
Ethylene bromide	C ₂ H ₄ Br ₂	187.44	131.45	1.14602	2.21324	1.98124	97.06
Ethylene chloriodide	C ₂ H ₄ ICl	189.84	140.1	1.15179	2.16439	1.87915	101.03
Ethylene chloride	CH ₂ ClCH ₂ Cl	98.68	83.5	1.10764	1.28082	1.15635	85.94
Ethene chloride	CH ₃ CHCl ₂	98.68	59.9	1.08538	1.20394	1.10923	88.96
Acetyl chloride	CH ₃ COCl	78.27	50.73	1.07640	1.13773	1.05698	74.05
Trichloroacetyl chloride	CCl ₃ COCl	181.38	118.0	1.14617	1.65640	1.44517	125.51
Chloral	CCl ₃ COH	147.01	97.2	1.11771	1.54480	1.3821	106.37
Pentachlorethane	CCl ₃ CHCl ₂	201.79	159.1	1.17008	1.70893	1.46052	138.2
Methene chloride	CH ₂ Cl ₂	84.71	41.6	1.05905	1.37776	1.30093	65.12
Chloroform	CHCl ₃	119.08	61.2	1.08362	1.52657	1.40877	84.53
Chloropierin	C(NO ₂)Cl ₃	164.01	111.9	1.13999	1.69225	1.48444	110.49
Carbon tetrachloride	CCl ₄	153.45	76.74	1.10268	1.63195	1.47999	103.68
Bromoform	CHBr ₃	252.22	151.2	1.16338	2.83413	2.43611	103.53
Trichlorobromomethane	CHBrCl ₂	197.83	104.07	1.12634	2.05496	1.82446	103.43
Propionitrile	C ₃ H ₅ CN	54.92	97.08	1.14270	0.80101	0.70098	73.35
Epichlorhydrin	CH ₂ ClCH ₂ OCH ₂	92.24	116.55	1.13861	1.20313	1.05667	87.29
Allyl alcohol	CH ₂ CHCH ₂ OH	57.87	96.6	1.11529	0.86990	0.77998	74.19
Acetone	CH ₃ COCH ₃	57.87	56.53	1.08609	0.81858	0.75969	76.78
Heptane	CH ₃ (CH ₂) ₅ CH ₃	99.79	98.43	1.14111	0.70048	0.61396	162.56
Ethyl-amy!	(CH ₃) ₄ CH(CH ₂) ₃ CH ₃	99.79	90.3	1.13126	0.69692	0.61606	161.98
Octane	CH ₃ (CH ₂) ₆ CH ₃	113.76	125.46	1.17693	0.71893	0.61077	186.26
Di-isobutyl	(CH ₃) ₂ CH(CH ₂) ₂ CH(CH ₃) ₂	113.76	108.53	1.15534	0.71110	0.61549	181.83
Aniline	C ₆ H ₅ NH ₂	92.83	183.7	1.18924	1.03790	0.87274	106.37
Picoline	CH ₂ =C=CH-CH ₂ -N	92.83	133.5	1.15497	0.96161	0.83258	111.50
Nitrogen tetroxide	N ₂ O ₄	92.06	21.6	1.03523	1.4903	1.43958	63.95
Silicon tetrachloride	SiCl ₄	169.48	57.57	1.08635	1.52408	1.40294	120.80
Titanium tetrachloride	TiCl ₄	189.48	136.4	1.15647	1.76041	1.52223	134.47

TABLE III (*continued*).

Substance.	Formula.	Mol. weight.	B. p. °.	Vol. at b. p.	Sp. gr. at 0°.	Sp. gr. at b. p.	Sp. vol.
Tin tetrachloride	SnCl_4	259.28	113.9	1.15197	2.27875	1.97813	131.07
Phosphorus trichloride	PCl_3	137.07	75.95	1.09827	1.61275	1.46845	93.34
Phosphorus tribromide	PBr_3	270.21	172.9	1.17140	2.92311	2.49541	108.28
Phosphoryl chloride	POCl_3	153.03	107.23	1.13378	1.71163	1.50967	101.37
Thiophosphoryl chloride	PSCl_3	169.05	125.12	1.14575	1.66820	1.45599	116.11
Phosphoryl bromochloride	POBrCl_2	197.41	137.6	1.15894	2.12065	1.83944	107.38
Ethoxyphosphorus chloride	$\text{PCl}_2\text{C}_2\text{H}_5\text{O}$	146.60	117.5	1.14509	1.30527	1.13989	128.61
Phosphenyl chloride	$\text{PCl}_2\text{C}_6\text{H}_5$	178.52	224.6	1.2252	1.3428	1.10415	161.68
Vanadyl trichloride	VOCl_3	173.27	127.19	1.14387	1.86534	1.63073	106.25
Arsenic trifluoride	AsF_3	131.9	60.4	1.08824	2.6659	2.4497	53.84
Arsenic trichloride	AsCl_3	181.0	130.21	1.14956	2.20500	1.91813	94.37
Thionyl dichloride	SOCl_2	118.68	78.8	1.10208	1.67673	1.52143	78.01
Sulphothionyl chloride	SSCl_2	134.70	138.12	1.14571	1.70941	1.49201	90.28
Chlorosulphonic acid	$\text{SO}_2\text{O.HCl}$	116.23	155.3	1.15238	1.78474	1.54874	75.05
Sulphuryl dichloride	SO_2Cl_2	134.64	69.95	1.09479	1.70814	1.56025	86.23
Disulphuryl chloride	$\text{S}_2\text{O}_5\text{Cl}_2$	214.50	189.59	1.15713	1.85846	1.60610	133.55
Chromyl dichloride	CrO_2Cl_2	155.06	115.9	1.11560	1.96101	1.75780	88.21
Carbon disulphide	CS_2	75.93	46.04	1.05704	1.29215	1.22242	62.11

weights of phosphorus, chromium, vanadium, arsenic and tin are probably known to within 0·2. The most doubtful members are titanium and antimony. Mendelejeff has already discussed the few determinations which have been made of the atomic weight of the former element, and he has concluded that the number hitherto assigned to it is probably too high by at least 2 units. An examination of the memoirs of Rose and Pierre, upon whose determinations the commonly accepted value of Ti depends, will serve to show that Mendelejeff's doubts are sufficiently well founded to render a fresh investigation on this subject very desirable. I have been induced to attack this question, as much for the sake of testing Mendelejeff's hypothesis as to the place of titanium in the system of the chemical elements, as for the knowledge which it is calculated to afford of the particular numerical value to be assigned to this metal. The investigation has proved more tedious than was anticipated, owing to the difficulty of finding a compound fulfilling all the conditions to be desired in a substance which is to serve for an atomic weight determination. I have therefore provisionally adopted Rose's number as modified by Mendelejeff. That considerations of the kind adduced by the Russian chemist in this particular instance ought to be accepted with caution is indicated by the analogous case of tellurium, which, according to Mendelejeff's classification, ought to be placed between iodine and antimony with an atomic weight of 125, whereas all experimental evidence goes to show that this value is too low by at least 2 units. The recent observations of Mr. W. L. Wills have proved that the atomic weight of tellurium is certainly not lower than 126·8, and is probably as high as 127·8, thus confirming the determinations of Berzelius and of von Hauer.

It seems highly probable that the number generally assigned to Sb, on the authority of Dumas and of Dexter, is too high by about 2 units. The value adopted by me is that recently determined by Professor J. P. Cooke, of Harvard, from a large and extremely concordant series of observations, made with various antimonial compounds. This value (120·0) agrees almost exactly with that found by Schneider, in 1856.

2. *Errors of Specific Gravity.*—These may be of two kinds: we may have in the case of a perfectly pure liquid errors of weighing, or in the determination of the temperature; or we may have in addition the effect of impurities in the compound. A careful revision of my observations leads me to conclude that the errors from the first named causes rarely exceed 1 in 10,000. And when regard is had to the very high degree of purity of the greater number of the liquids experimented upon, I am disposed to believe that the value given represents the true specific gravity in the great majority of cases to within 0·1 per cent.

As a rule the inorganic compounds could be readily obtained pure. Preparations of phosphoryl chloride, for example, whether made by the action of oxalic acid or of boric acid upon the pentachloride, or by heating this substance with the pentoxide, had identical specific gravities. This is, of course, not equally true of bodies separated by fractional distillation, but with due care and by operating on large quantities, the effect of possible admixture becomes extremely small; as an instance I may refer to the case of ethidene chloride given on p. 186; two samples of this liquid, obtained by distinctly different methods, one of which necessitated long continued fractionation, afforded results which differed by only 0.08 per cent. The observations, as it happened, were absolutely independent; they were made in both cases in duplicate, with different bottles, thermometers, balances, and weights.

3. *Errors in the Determination of the Thermal Expansion.*—I have already sought to prove by direct experiment that the dilatometrical method of determining the expansion of a liquid is calculated to afford a trustworthy result. The observations on water, given on p. 171, were undertaken expressly to test this point. The indications of the dilatometer depend, of course, upon several observational magnitudes, but I am unable to discover any evidence for the existence of any constant errors which would exert a preponderating influence in a special direction. A properly calibrated dilatometer, of which the rate of expansion is known, will afford results identical with those furnished by absolutely independent methods, such as that of displacement, as employed by Hagen and by Matthiessen. I have also sought to show that the method of correcting for the cooled portion of the liquid contained in the stem introduces no sensible error in the result; the observations obtained in the water-bath, when the whole of the liquid was of uniform temperature, are practically identical with those afforded by the oil-bath as corrected, where a considerable portion of the liquid in the stem possessed a much lower temperature than that in the bulb.

The discrepancy in my own determinations of the relative volume of a liquid at any temperature between 0° and its boiling point may be set down as 1 in 10,000. That two preparations of the same liquid, even when obtained by perfectly independent methods, do actually show identical rates of thermal expansion may be seen from the example, already quoted, of ethidene chloride, given on p. 186. Additional instances might be adduced in the cases of phosphoryl and thiophosphoryl chlorides, and of iodine monochloride.

4. *Errors in the Determination of the Boiling Point.*—I have already detailed the precautions which I adopted to ascertain the boiling points of the liquids experimented upon. All the known sources of error,

such as overheating, succussion, &c., were carefully guarded against. The reduction to the standard pressure is, of course, arbitrary, inasmuch as it assumes the validity of Dalton's law, but the error thereby introduced may be neglected, on account of the small range of barometric pressure; the boiling points are certainly more nearly comparable than they would have been had no such correction been applied. There is one possible source of error, of which so far as I know, no heed has yet been taken in determinations of this character, and that is, the influence of radiation. Lothar Meyer has already directed attention to this point, but experimental evidence as to the magnitude of its action is altogether wanting. I find that a thermometer, of which the bulb is surrounded by black cloth or caoutchouc tubing, when placed in steam, invariably reads a few tenths of a degree higher than when the bulb is in immediate contact with the vapour, but my observations are at present too few in number to enable me to state to what this phenomenon is actually due. I think, however, that it can hardly be attributed to pressure on the bulb.

In the absence of proper data it is impossible to give any precise estimate of the amount of error which may affect the determinations of the boiling points of the liquids. When it is borne in mind that nearly all the bodies were of comparatively low boiling point (40 out of the 47 liquids boiling between 46° and 140°), and that the majority of these could readily be obtained of a high degree of chemical purity, I should suppose that the determinations cannot be affected with an error so considerable as 1° . Let us assume, however, that such an error was possible, and on the basis of this and of the former estimations, let us seek to determine the effect of these errors on the determination of the specific volume.

Let σ be the specific volume, W the molecular weight, and s the specific gravity of the substance at the boiling point. Then—

$$\sigma = \frac{W}{s}.$$

If further S_0 be the specific gravity at 0° , and V_0 and V be the volumes at 0° and at the boiling point respectively, the above relations may be written—

$$\sigma = \frac{WV}{S_0 V_0} \text{ or } \frac{WV}{S_0} \text{ if } V_0 = 1.$$

Hence if $\delta\sigma$ be the error in σ , and a similar notation be used for the other quantities, and if we suppose all the errors to be of such sign that they tend to alter the value of σ in the same direction, then—

$$\delta\sigma = \frac{\delta W}{S} + \sigma \left\{ \frac{\delta S_0}{S_0} + \frac{\delta V}{V} \right\}.$$

δV consists of two parts, the first depending on the inaccuracy in

the knowledge of the law of expansion; the second on that of the determination of the boiling point. If α be the coefficient of expansion of the substance at the boiling point t , we may put

$$\delta V = \delta \sigma + \alpha \delta t.$$

If, further, we assume that for all the liquids $\delta S_0 = \cdot 001$ and $\delta V = \cdot 0001$, then—

$$\delta \sigma = \frac{\delta W}{S} + \frac{\sigma}{1000} \left\{ \frac{1}{S_0} + \frac{1}{10V} \right\} + \frac{\sigma \alpha \delta t}{V}.$$

Taking the estimations given on pp. 372 and 373 for the errors of atomic weight, I have calculated the effect on the determination of the specific volume in the cases of a number of the liquids, and in no instance does it amount to a unit.

Thus in the case of bromine—

$$\delta \sigma = \frac{\cdot 1}{3} + \cdot 053 \left\{ \frac{1}{3} + \frac{1}{10\cdot 7} \right\} + \frac{53 \times \cdot 00116}{1\cdot 07} = 0\cdot 11.$$

In that of chloropicrin—

$$\delta \sigma = \frac{\cdot 35}{1\cdot 5} + \cdot 110 \left\{ \frac{1}{1\cdot 7} + \frac{1}{11\cdot 4} \right\} + \frac{110 \times \cdot 00124}{1\cdot 14} = 0\cdot 42.$$

In the case of phosphorus trichloride—

$$\delta \sigma = \frac{\cdot 35}{1\cdot 5} + \cdot 093 \left\{ \frac{1}{1\cdot 6} + \frac{1}{11\cdot 0} \right\} + \frac{76 \times \cdot 0013}{1\cdot 1} = 0\cdot 39.$$

In that of phosphoryl monochloride—

$$\delta \sigma = \frac{\cdot 4}{1\cdot 8} + \cdot 107 \left\{ \frac{1}{2\cdot 1} + \frac{1}{11\cdot 6} \right\} + \frac{107 \times \cdot 00116}{1\cdot 16} = 0\cdot 39.$$

It will be seen that the uncertainty respecting the molecular weight of the compound has usually the greatest effect upon the value for the specific volume.

In the case of isomeric compounds the specific volumes of which are to be compared together, it is unnecessary to take into account the possible errors of atomic weight. It may be shown that the observed difference, for example, between ethidene chloride and ethylene chloride is considerably greater than can be accounted for by experimental errors.

But whatever may be the final effect of the various errors incidental to this method of determining the specific volume of a liquid substance, it is certain that the results are sufficiently precise to permit of trustworthy conclusions being drawn as to the connection between the specific gravity of such bodies and their molecular weights and chemical constitution. One proof of this is afforded by the fact that

different observers working by independent, and in some cases very dissimilar methods, and upon substances of very different origin, have obtained substantially identical results. It will have been noticed in the course of the paper, that the specific gravities, boiling points, and rates of thermal expansion of a certain number of the liquids which have served me for purposes of comparison, have already been determined, more particularly by Pierre and Kopp. I have calculated from the data furnished by their observations, the specific volumes of these liquids, assuming for their molecular weights the numbers given in Table III.

I will first compare my results with those of Pierre; these it will be observed mainly refer to inorganic substances, and more particularly to combinations containing chlorine and bromine.

	Specific volume.	
	Pierre.	Thorpe.
Bromine.....	53·72	53·48
Phosphorus bromide	108·35	108·28
Silicon tetrachloride.....	121·48	120·80
Titanium chloride.....	124·32	124·47
Tin tetrachloride	132·03	131·07
Phosphorus chloride.....	93·48	93·34
Arsenic chloride	94·61	94·37
Carbon bisulphide.....	62·23	62·11

It will be noticed that the agreement is remarkably close; the difference in the extreme case (that of tin tetrachloride) is about 0·7 per cent., and in mean it is only about 0·2 per cent. As a rule Pierre's numbers are slightly greater than mine; this is probably due to the circumstance that his determinations of boiling points are usually higher, owing to the fact of the thermometer bulb being placed in the heated liquid, and not in its vapour. This would tend to give a lower number for the specific gravity at the boiling point, and therefore a higher value for the specific volume.

Of the organic compounds investigated by Pierre, the following also serve for comparison with my results:—

	Specific volume.	
	Pierre.	Thorpe.
Ethylene chloride.....	85·45	85·34
Ethylene bromide.....	97·70	97·06
Chloroform	84·63	84·53
Carbon tetrachloride	103·98	103·68

In all the above instances Pierre's numbers are slightly in excess of

mine, but the extreme difference is not greater than in the former series, and on the average is less than 0·3 per cent.

Comparatively few of the large number of substances investigated by Kopp are available for the purpose of direct comparison with the results of my observations. The following, however, may be quoted:—

	Specific volume.	
	Kopp.*	Thorpe.
Acetyl chloride	74·95	74·05
Acetone	77·09	76·78
Aniline	105·99	106·37
Di-isobutyl	184·50	184·83

The greatest difference here (1·2 per cent.) is in the case of acetyl chloride, and this is mainly attributable to the higher boiling point (55—56°) and lower specific gravity observed by Kopp, due probably to a slight admixture of acetic anhydride, which seems to be invariably formed in the preparation of this compound by Gerhardt's method.

Buff, in the course of the observations made to test his hypothesis as to the connection between the specific volume of an element, and its atomic value (*Ann. Chem. Pharm.*, Suppl. 4, 129), determined the specific gravity of phosphorus and phosphoryl chlorides at various temperatures. His observations at the boiling points of these liquids furnish results which are almost identical with mine.

	Specific volume.	
	Buff.	Thorpe.
Phosphorus chloride	93·33	93·34
Phosphoryl chloride	101·41	101·37

IV. CONCLUSIONS.

Having thus, I hope, succeeded in proving that the numbers contained in the last column of Table III may be legitimately considered as denoting with approximate accuracy the specific volumes of the respective liquids, I proceed to indicate the conclusions which may be based upon them.

1. I cannot regard it as absolutely proved that isomeric liquids of the same chemical type, using that phrase in the sense in which Kopp employs it, have invariably the same specific volume. It is certain, for example, that ethidene chloride and Dutch liquid have not the

* Kopp's specific gravities are referred to water at 0°, instead of at 4°. The effect of this difference is, however, unimportant.

same specific gravity at their boiling points, and accordingly have not the same specific volume. The observations have given for—

	Specific gravity at boiling point.	Specific volume.
Ethylene chloride.....	1.15635	85.34
Ethidene chloride.....	1.10923	88.96
		<hr/>
	Difference..	3.62

This difference of 3.62 cannot be fairly attributed to errors of observation. The agreement of my observations with those of Pierre in the case of ethylene chloride, and the very concordant results obtained from the two independent series made with ethidene chloride, seem to me to leave no room for doubt on this point.

The specific volumes of ethylene chloride and of its analogues, $C_2H_4Br_2$ and C_2H_4ICl , are considerably below the numbers calculated by means of Kopp's values.

	Observed.	Calculated.	Diff.
Ethylene chloride	85.3	89.5	4.2
„ bromide....	97.1	99.5	2.4
„ chloridide..	101.0	104.2	3.2

The experimental evidence, so far as it goes, seems to show that the normal hydrocarbons have a lower specific gravity at their boiling points, and hence have a greater specific volume than their isomerides. But this evidence at present hardly goes far enough to permit of a definite conclusion: we require a much larger number of observations made upon hydrocarbons of different homologous series. Unfortunately, however, these bodies are very difficult to obtain pure.

The mean difference between the specific volume of heptane and octane, and of ethyl-amyl and di-isobutyl is (including Kopp's number for the latter substance) 22.7, which is very near the mean value given by Kopp, viz., 22, for an increment of CH_2 .

It is, of course, quite possible that the specific volumes of carbon and hydrogen may be slightly modified by the mode in which the atoms are grouped in a compound: that we may have, in fact, variations of a kind similar to that which Gladstone, and, more recently, Brühl have shown to exist in the atomic refraction of carbon, dependent on the manner of its combination. Indeed it is not improbable that an intimate connection exists between the refractive power of such compounds and their specific volumes. Landolt has inferred that differences of molecular grouping in no way affect the refractive index of the constituent atoms, and Gladstone has shown that as a general law the molecular refractive power of a body is equal to the sum of the refraction of the atoms, just as it has been inferred that the

specific volume of carbon is invariable, and that the specific volume of a compound liquid is equal to the sum of the specific volumes of its constituent elements or compound radicles. Exceptions, however, are known to this law: thus the molecular refraction of many benzene derivatives, ethereal oils, and terpenes, and other bodies relatively rich in carbon is considerably greater than that calculated from their atomic refractions. Brühl has succeeded in detecting the relation between the constitution of these bodies and their optical character: he has shown that their refractive power depends upon the mode of combination of the constituent atoms; it appears, for example, that in the case of unsaturated bodies the atoms, which are more than once directly united to each other, exert a greater influence in propagating light than atoms which with the same atomic value are united to other atoms. Gladstone has pointed out that isomeric bodies occasionally differ widely in their optical properties: thus aniline and picoline, each C_8H_7N , have totally different refraction equivalents. It is also certain that they have totally distinct specific volumes, thus:

	Aniline.	Picoline.
Kopp.....	106.0	—
Thorpe	106.4	111.5

It may be further noted that a large number of those bodies, of which the molecular refraction is greater than the computed value, have also a specific volume considerably less than the calculated numbers. The specific gravity, boiling point, and rate of thermal expansion of benzene are known with great accuracy from the experiments of Kopp (*Jahresb.*, 1847-8, 65); Longuinine (*Jahresb.*, 1867, 48); Pisati and Paternò (*Chem. Soc. J.* [2], 12, 686); and Adrieenz (*Ber.*, 6, 442); and from their observations I have calculated the specific volume of this liquid with the following results:—

Kopp	95.94
Longuinine.....	95.98
Pisati and Paternò	95.94
Adrieenz.....	95.90
<hr/>	
Mean	95.94
Calculated specific volume ..	99.0

The observed values it will be noticed are extremely concordant, but they differ by more than 3 per cent. from the computed value. Differences of the same order are exhibited by a number of aromatic compounds; I select the following from Kopp's observations:—

	Specific volume.		Difference between observed and computed.
	Observed.	Computed.	
Phenol.....	103·6	106·8	+ 3·2
Benzyl alcohol	123·7	128·8	+ 5·1
Benzoic acid	126·9	130·0	+ 3·1
Benzyl aldehyde....	118·4	122·2	+ 3·8
Cymene	183·5	187·0	+ 3·5
Naphthalin	149·2	154·0	+ 4·8

It might certainly be inferred from these observations that CH_2 has a different value in the benzene derivatives from that which it possesses in organic compounds generally.

Our views as to the constitution of the aromatic compounds would lead us to expect that the specific volume of benzene (and the derivative in which the benzene group functions) would in all probability be different from that deduced from observations made for the most part on compounds of totally different constitution. Kopp (*Ann. Chem. Pharm.*, Supp. 5, 303) has shown from Longuinine's observations, that, whilst benzene has an abnormally low specific volume, its homologues show the constant increase of 22 in the volume for an increment of CH_2 , which is what might be anticipated, since these bodies are produced by the addition (substitution) of methyl, ethyl, &c., to the benzene group.*

Indeed other values have been calculated for carbon and hydrogen: Lothar Meyer makes $\text{H} = 3$, and Loschmidt $\text{C} = 14$ and $\text{H} = 3·5$, and by assuming that half the carbon atoms in benzene have the value 11, and the remainder the value 14, and that hydrogen has the constant value 3·5, we obtain a calculated value for this hydrocarbon which is identical with the observed number: $(11 \times 3) + (14 \times 3) (3·5 \times 6) = 96·0$.

It would be interesting to determine how far such a dissimilarity in the specific volumes of the carbon atoms, or of the CH groups in benzene, is in harmony with the dynamical conceptions of the constitution of this hydrocarbon which we owe to Kekulé and to Ladenburg.

* I may be allowed to quote the following from Oscar Meyer's *Die Kinetische Theorie der Gase*:— . . die Form der Molekel und die Gruppierung der atome in derselben kann Einfluss auf den in Minimum erforderlichen Raum haben. Ein platte Molekel mit nahezu in einer Ebene neben einander gelagerten Atomen wird wenn die bei ihnen, von der Wärme veranlaesten Bewegungen sich dreht, mehr Raum beanspruchen, als eine Kugelförmige Molekel mit enger zusammengedrängten Atomen. So ist es . . . leicht erklärlich, dass den Atomen je nach ihrer Stellung in der Molekel eine verschiedene Raumerfüllung zugeschrieben werden darf. *Art. Molecular-Volumen*, p. 218.

I would also here recall to mind Jungfleisch's observations on the specific volumes of the chlorine substitution products of benzene. From these it is evident that the positions of the chlorine atoms affect in a very marked manner the specific volume of the product. (*Compt. rend.*, 64, 911).

The only aromatic compounds contained in the table given on p. 144 are aniline and the phosphenyl chloride of Michaelis. The probable specific volume of the former liquid cannot be very accurately computed on account of the uncertainty which attaches to the particular value of the nitrogen atom in this compound. I found the specific volume of aniline to be 106·4, which is identical with Kopp's determination, but it happens that this very number was employed by Kopp to calculate the probable value of N in this class of compounds.

Phosphenyl chloride, $\text{PCl}_2\cdot\text{C}_6\text{H}_5$, however, resembles the other aromatic compounds in possessing a lower specific volume than the computed value.

Observed sp. vol. $\text{PCl}_2\cdot\text{C}_6\text{H}_5$	161·7
Calculated $(25\cdot3 + 45\cdot4 + 66 + 27\cdot5) =$	164·2
	<hr/>
Difference ..	2·5

The estimated values of P and Cl are those given on pp. 384 and 387, those for C and H are due to Kopp.

2. My observations furnish additional evidence in support of the assumption already regarded by Kopp and others as highly probable that an element or a compound radicle occupies the same volume in combination as in the free state. I find, by direct observation, that the specific volume of nitrogen tetroxide is 64, hence $\text{NO}_2 = 32$. The specific volume of chloroform is 84·5 : that of chloropicrin is 110·5. Chloropicrin may be regarded as derived from chloroform by the substitution of an atom of hydrogen by an equivalent amount of NO_2 .

Hence we have—

Specific volume $\text{C}(\text{NO}_2)\text{Cl}_3$	110·5
„ CHCl_3	84·5
	<hr/>
	26·0
Add specific volume of H	5·5
	<hr/>
Calculated volume of NO_2	= 31·5
Observed „ „	32·0

Similar evidence is afforded by ethylene bromide and ethylene chloridide. If we deduct the specific volume of C_2H_4 , calculated by means of Kopp's values, from the observed specific volumes of ethylene bromide and ethylene chloridide, we obtain numbers which are

nearly equal to the specific volumes of bromine and of iodine monochloride as determined by experiment.

		Sp. vol. Br.	
Mean sp. vol. $C_2H_4Br_2$.*		Calculated.	Observed (mean).*
97·38	— 44	53·38	53·60
		Sp. vol. ICl.	
Sp. vol. C_2H_4ICl .		Calculated.	Observed.
101·03	— 44	57·03	56·2

We have a like instance in the case of propionitrile, C_2H_5CN . The specific volume of this compound is 78·4: subtracting the calculated volume of C_2H_5 , viz., 49·5, we obtain 28·9 as the specific volume of CN, which is identical with the number calculated by Kopp from Faraday's observations.

3. *Determination of the Specific Volumes of Certain Elements.—Chlorine.*—The replacement of an atom of hydrogen by an atom of chlorine in a liquid is accompanied by an increase in the specific volume of about 17·2, hence specific volume of Cl $17 + 5·5 = 22·7$. Thus in the case of trichloroacetyl chloride and acetyl chloride—

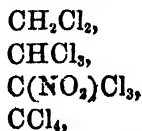
Specific volume of CCl_3COCl	=	125·5
„ „ CH_3COCl	=	74·0
			<hr/>
		3)	51·5
			<hr/>
			17·2
Add specific volume of H		5·5
			<hr/>
Specific volume of Cl	=	22·7

So also in the case of ethylene and ethidene chloride and pentachloroethane.

Specific vol. of CCl_3CHCl_2 ..	=	138·2	CCl_3CHCl_2	=	138·2
„ „ CH_3CHCl_2 ..	=	88·9	$CH_2Cl.CH_2Cl$	=	85·3
		<hr/>			<hr/>
		3)	49·3	3)	52·9
			<hr/>		<hr/>
			16·4		17·6
Add specific volume of H.....	5·5			Add sp. vol. of H	5·5
	<hr/>				<hr/>
	21·9				23·1

Mean specific volume of Cl..... 22·5

The mean value of Cl calculated from the series—



* Pierre's number included.

is in like manner found to be 22.5. I have included Pierre's results in the calculation.

On the assumption that the specific volume of $\text{CH}_2 = 22$, and that an atom of carbon replaces two atoms of hydrogen without alteration in volume, my observations furnish me with the following estimations of the specific volume of Cl:—

From ethidene chloride.....	22.5
„ acetyl chloride.....	23.3
„ trichloracetyl chloride	22.7
„ chloral	22.9
„ methene chloride.....	21.6
„ chloroform	22.7
„ chloropicrin	22.5
„ carbon tetrachloride	23.2
Mean.....	22.68

Hence the specific volume of Cl may be taken as 22.7.

Bromine.—The specific volume of bromine appears to be about 28.1. It is found that when an atom of chlorine is replaced by an atom of bromine there is an increase of about 6 in the specific volume.

Specific volume of CHBr_3	103.53
„ „ CHCl_3	84.53
	3) 19.00
	6.3
Add specific volume of Cl	22.7
Specific volume of Br..... =	29.0
From phosphoryl bromochloride and trichloride—	
Specific volume of POBrCl_2	107.38
„ „ POCl_3	101.37
	6.01
Add specific volume of Cl	22.7
Specific volume of Br..... =	28.7
From phosphorus tribromide and trichloride—	
Specific volume of PBr_3	108.31
„ „ PCl_3	93.41
	3) 14.90
	5.0
Add specific volume of Cl	22.7
Specific volume of Br..... =	27.7

The replacement of an atom of hydrogen by one of bromine is accompanied by an increase of 23·9 in the specific volume of the compound. Thus in the case of trichlorobrommethane and chloroform—

Specific volume of CBrCl_3	108·43
„ „ CHCl_3	84·53
	<hr/>
	23·90
Add specific volume of H	5·5
	<hr/>
Specific volume of Br	= 29·4

When NO_2 replaces Br in a liquid there is an increase of about 2 in the specific volume of the compound. Thus from trichlorobrommethane and chloropicrin—

Specific volume of $\text{C}(\text{NO}_2)\text{Cl}_3$	110·49
„ „ CBrCl_3	108·43
	<hr/>
	2·06

And $31·5 - 2·1 = 29·4$ sp. vol. of Br.

Assuming Kopp's values for C and H, my observations furnish the following additional estimations of the specific volume of Br:—

From ethylene bromide	26·7
„ bromoform	29·0
„ chlorobrommethane	29·0

The mean value deduced from all the observations is 28·1. These numbers it will be observed are in close accordance with those already calculated by Kopp, viz., Cl 22·8 and Br 27·8.

Fluorine.—From arsenic fluoride and arsenic chloride—

Specific volume of AsCl_3	94·37
„ „ AsF_3	53·84
	<hr/>
	3)40·53
	<hr/>
	13·51

It appears that when an atom of fluorine is replaced by one of chlorine an increase of 13·5 results in the specific volume. Hence the specific volume of F is $22·7 - 13·5 = 9·2$.

Iodine.—The observations with iodine monochloride and ethylene chloriodide furnish the number 36·0 as the specific volume of iodine. This value differs slightly from the value 37·2 (recalculated),* deduced from Kopp and Pierre's observations. The data, however, are insufficient to ascertain the true volume: the expansion of only 6 liquids containing iodine seems to have been determined.

* The atomic weight of iodine was taken by Kopp as 127·1.

By the aid of these values we are able to calculate the specific volume of a number of elementary bodies. We will first take the members of the tetrad group, silicon, titanium, and tin.

Silicon.—From silicon tetrachloride—

	Pierre.	Thorpe.
Specific volume of SiCl_4	121.5	120.8
Less specific volume Cl_4	90.8	90.8
	<hr/> 30.7	<hr/> 30.0

The mean specific volume of Si is 30.3.

Titanium.—From titanium tetrachloride—

	Pierre.	Thorpe.
Specific volume of TiCl_4	124.3	124.5
Less specific volume Cl_4	90.8	90.8
	<hr/> 33.5	<hr/> 33.7

The mean specific volume of Ti is therefore 33.6.

Tin.—From tin tetrachloride—

	Pierre.	Thorpe.
Specific volume of SnCl_4	132.0	131.1
Less specific volume Cl_4	90.8	90.8
	<hr/> 41.2	<hr/> 40.3

The mean specific volume of Sn is 40.8.

These observations show that Kopp's supposition (*Ann. Chem. Pharm.*, **96**, 319), that members of the same family of elements have probably identical specific volumes is not confirmed by experiment. *The specific volume of the element appears to be a function of its atomic weight.*

Evidence of the same fact is afforded by the specific volumes of phosphorus, arsenic, and antimony.

Phosphorus.—From phosphorus trichloride—

	Pierre.	Thorpe.	Buff.
Specific volume of PCl_3 . . .	93.5	93.3	93.3
„ „ „ Cl_3	68.1	68.1	68.1
	<hr/> 25.4	<hr/> 25.2	<hr/> 25.2

From phosphorus tribromide—

	Pierre.	Thorpe.
Specific volume of PBr_3 . .	108.4	108.3
„ „ „ Br_3	84.3	84.3
	<hr/> 24.1	<hr/> 24.0

From phosphoryl chloride—

	Buff.	Thorpe.
Specific volume of POCl_3 .	101·4	101·4
Less (7·8 + 68·1) ..	75·9	75·9
Specific volume of P = ..	25·5	25·5
From thiophosphyl chloride—		
Specific volume of PSCl_3		116·1
Less (68·1 + 22·6)		90·7
Specific volume of P =		25·4
From phosphoryl bromochloride—		
Specific volume of POBrCl_2		107·4
Less (45·4 + 28·1 + 7·8)		81·3
Specific volume of P =		26·1
From ethoxyphosphorus chloride—		
Specific volume of $\text{PCl}_2 \cdot \text{C}_2\text{H}_5\text{O}$		128·6
Less (45·4 + 57·3)		92·7
Specific volume of P =		25·9
The mean of the 10 estimations is 25·3.		

Arsenic.—From arsenic trichloride—

	Pierre.	Thorpe.
Specific volume of AsCl_3	94·6	94·4
Less Cl_3	68·1	68·1
	26·5	26·3

From arsenic fluoride—

Specific volume of AsF_3	53·8
Less F_3	27·6
	26·2

The mean of these values is 26·3.

Antimony.—I have recalculated the specific volume of antimony tri chloride from Kopp's observations on the assumption that the atomic weight of Sb is 120, and that of Cl is 35·37.

According to Kopp, antimony trichloride boils at 223° , under a pressure of 747·7 mm. Reduced boiling point $223·5^\circ$. Its expansion by heat may be expressed by the formula—

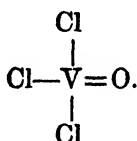
$$V = 1 + 0·000\ 805\ 4\delta + 0·000\ 010\ 32\delta^2,$$

in which δ = number of degrees above the melting point of the body $73·2$ (Kopp). Its specific gravity at $73·2^\circ$ compared with water at

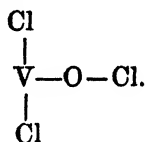
4° is 2·6753, at $223\cdot5$ it is 2·3377. Accordingly its specific volume = $\frac{226\cdot11}{2\cdot3377} = 96\cdot72$.

Hence we have for the specific volume of Sb $96\cdot7 - 68\cdot1 = 28\cdot6$.

Vanadium.—The specific volume of this element, as deduced from vanadyl trichloride, depends upon the constitution which is assigned to this compound; and this, in its turn, depends upon the particular atomic value which vanadium is supposed to exert on it. If vanadium be pentad, VOCl_3 must be written—



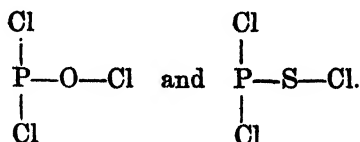
If triad, then it must be written—



In a former paper (*Proc. Roy. Soc.*, 160, 1875), I have shown that the specific volumes of phosphoryl trichloride and thiophosphoryl chloride indicate that phosphorus is a triad in these compounds. When oxygen is united to an element by both its affinities, its specific volume is 12·2: when it is attached by only one, its volume is 7·8, a difference of 4·4. Sulphur in like manner has two values, viz., 28·6 and 22·6 — a difference of 6·0.

The specific volume of POCl_3 is	101·3
Subtract $\text{PCl}_3 = (25\cdot3 + 68\cdot1) \dots$	93·4
Specific volume of O	7·9
The specific volume of PSCl_3 is	116·1
Subtract PCl_3	93·4
	22·7

Hence phosphoryl trichloride and thiophosphoryl chloride must be written—



If now vanadyl trichloride be regarded as possessing a similar

constitution to phosphoryl chloride, the specific volume of vanadium is 30·4—

Specific volume VOCl_3	106·3
Less 7·8 + 68·1.....	75·9
	<hr/> 30·4

If, however, it be regarded as pentad it is 26·0—

Specific volume VOCl_3	106·3
Less 12·2 + 68·1	80·3
	<hr/> 26·0

Sulphur.—The specific volumes of thionyl chloride and sulphothionyl chloride show that these bodies have an analogous constitution,

viz., $\text{SO} \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$ and $\text{SS} \begin{Bmatrix} \text{Cl} \\ \text{Cl} \end{Bmatrix}$.

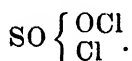
Specific volume of SSCl_2	90·3
Less Cl_2	45·4
	<hr/> 2)44·9

Specific volume of S

Specific volume of SOCl_2	79·1
Less SCl_2	67·9
	<hr/> 11·2

Specific volume of O

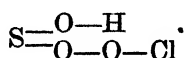
It would also appear from the specific volume of sulphuryl dichloride that the constitution of this compound must be expressed as—



Specific volume of SO_2Cl_2	86·3
„ „ SOCl_2	79·1
	<hr/>

Specific volume of O

On the other hand all the oxygen atoms in chlorosulphonic acid have apparently the same specific volume, and hence this body has the constitution—



Thus $22·6 + 3(7·8) + 5·5 + 22·8 = 74·3$

Observed specific volume .. = 75·0

Buff has determined the specific gravity of sulphuric anhydride at 46—47°, and found it in two concordant experiments to be 1·8103. This gives 44·2 as the specific volume of this substance, a number

which agrees fairly well with that calculated from the specific volume of chlorosulphonic acid, viz., 46·0. This result is confirmatory of the view of the constitution of chlorosulphonic acid, that it is an addition-product of SO_3 and HCl .

The specific volume of disulphuryl chloride appears to indicate that one of the oxygen atoms has the value 12·2, whilst the remaining four have the value 7·8. Thus—

$$(22\cdot5) + 12\cdot2 + 4(7\cdot8) + 2(22\cdot7) = 133\cdot8$$

$$\text{Observed specific volume } \text{S}_2\text{O}_4\text{Cl}_2 = 133\cdot6$$

The specific gravity, boiling point, and rate of thermal expansion of carbon bisulphide have been already observed by Pierre and Buff, and the results lead to the following series of very concordant determinations of specific volume—

Pierre	62 23
Buff	62·17
Thorpe	62·11
	<hr/>
Mean	62·19

These numbers indicate that the two sulphur atoms in carbon bisulphide occupy different volumes. Thus—

$$\begin{array}{l} \text{C} + \text{S} + \text{S}' \\ 11 + 22\cdot6 + 28\cdot6 = 62\cdot2. \end{array}$$

It would be interesting to compare this compound with some of the organic thiocarbonates and with thiocarbonyl chloride, CSCl_2 . A comparison too between ethyl xanthate, $\text{CS} \left\{ \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{OC}_2\text{H}_5 \end{array} \right.$ and carbonyl disulpho-diethyl, $\text{CO} \left\{ \begin{array}{l} \text{SC}_2\text{H}_5 \\ \text{SC}_2\text{H}_5 \end{array} \right.$, obtained by the action of sulphuric acid on ethyl sulphocyanate, would doubtless be of value.

Buff (*Jahresb.*, 1868, 652) has determined the specific gravity of ethyl sulphocyanate at its boiling point, 146° : he found 0·8701 and 0·8694, mean 0·8697. This gives the specific volume 100·1, agreeing almost exactly with the calculated number—

$$\begin{array}{l} \text{C}_2\text{H}_5\text{.CN.S.} \\ 22 + 27\cdot5 + 28\cdot9 + 22\cdot6 = 101\cdot0. \end{array}$$

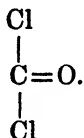
My determination of the specific volume of propionitrile, $\text{C}_2\text{H}_5\text{CN}$, gave 78·4 and $78\cdot4 + 22\cdot6 = 101\cdot0$.

Emmerling and Lengyel found that carbonyl chloride, the analogue of CSCl_2 , boiled at 8° , and had a specific gravity of 1·432 at 0° (*Ann. Chem. Pharm.*, Suppl. 7, 101). The determination is so close to the temperature at which the substance boils that we may take the

specific gravity at that temperature as 1·43 without sensible error. Hence we have for the specific volume $\frac{98\cdot67}{1\cdot43} = 68\cdot9$.

Observed specific volume of COCl_2	68·9
Less specific volume CCl_2	56·6
Volume of O	<hr/> 12·3

Since, as has been shown, the specific volume of oxygen united to an element by both its affinities is 12·2, this would indicate that the constitution of phosgene gas is—



in accordance with the generally received opinion. By analogy, therefore, the sulphur atom in thiocarbonyl chloride and in the thiocarbonates should possess the volume 28·6.

Kopp has already observed that the two atoms of oxygen in sulphur dioxide appear to occupy different volumes. According to Pierre the thermal expansion of sulphur dioxide may be expressed by the formula—

$$V = 1 + 0\cdot001\,496d + 0\cdot000\,022\,337\,5d^2 - 0\cdot000\,000\,495\,759d^3.$$

$$d = t - 25\cdot85.$$

Its specific gravity at $-20\cdot5^\circ$ was 1·4911, and its boiling point -8° . Hence its specific gravity at the boiling point is 1·455, and its specific volume 43·9.

$$\text{Calculated vol. } 22\cdot6 + 12\cdot2 + 7\cdot8 = 42\cdot6.$$

Andréeff (*Ann. Chem. Pharm.*, **111**; *Ann. Chem. Phys.* [3], **56**, 317), found that sulphur dioxide boils at -10° : its specific gravity at 0° compared with water at the same temperature is 1·4333, and the variation in its specific gravity by temperature may be expressed by the formula—

$$1\cdot4333 - 0\cdot002\,769t - 0\cdot000\,000\,271t^2.$$

From these numbers we obtain the specific volume 43·8.

That the atom of sulphur in the free state occupies the same volume as in combination is shown by Dr. Ramsay's observations. As a mean of several experiments he found the specific gravity of this body at its boiling point (446°) to be 1·4799, which gives the value 21·6 (*loc. cit.*).

Chromium.—The results of the observations on chromyl dichloride, CrO_2Cl_2 , allow of a determination of the specific volume of this element

on the supposition that the compound has a constitution analogous to that of sulphuryl dichloride, SO_2Cl_2 .

Specific volume of CrO_2Cl_2	88·2
„ „ SO_2Cl_2	86·3
	<hr/>
	1·9
Add specific volume S	22·6
	<hr/>
Specific volume of Cr =	24·5

Dr. Ramsay found that the specific gravity of chromyl dichloride at its boiling point was 1·7538; this gives the specific volume 88·4, which agrees closely with the above result.

If now we arrange the elements in the order of their atomic weights, as in the following table (p. 393), the connection between their specific volumes and these weights becomes apparent.

The main conclusions which I venture to draw from my observations may be briefly stated as follows:—

1. It seems certain that many isomeric liquids, even of the same chemical type, have not identical specific gravities at their respective boiling points, and hence have not identical specific volumes. Such exceptions are more commonly met with in compounds containing carbon and hydrogen: this fact appears to indicate that the specific volume of one or both of these elements is not absolutely invariable. Benzene derivatives especially show a greater departure from the general law than can be fairly attributed to experimental error. Their variations are of the same order as has been shown to occur in the refraction values for these compounds.

2. We must also suppose that of the additional elements, oxygen, sulphur, and nitrogen, have likewise variable specific volumes in conformity with Kopp's conclusions.

3. There is at present no experimental evidence for assuming that any other element has a variable specific volume.

4. Hence in the case of these elements the volume is not modified by the number of the atoms of the particular element in the molecule, and it is therefore altogether independent of the general complexity of the molecule.

5. The different members of a family of elements do not possess identical specific volumes: the volumes of the elements are periodic functions of their atomic weights.

6. The inquiry affords no evidence in support of the hypothesis that the specific volume of an element in combination is modified by any possible variation in the affinity-value which it may possess. The

<i>Atomic Weights.</i>					
I.	II.	III.	IV.	V.	VI.
H = 1	C = 11.97	Si = 28.0	Ti = 48		Sn = 117.8
	N = 14.01	P = 30.96	V = 51.2	As = 74.9	Sb = 120.0
	O = 15.96	S = 31.98	Cr = 52.4		
	F = 19.0	Cl = 35.47		Br = 79.75	I = 126.53
<i>Specific Volumes.</i>					
I.	II.	III.	IV.	V.	VI.
H = 5.5	C = 11.0	Si = 30.3	Ti = 33.6	—	Sn = 40.8
	N = (?)	P = 25.3	V = 30.4 (26.0)	As = 26.3	Sb = 28.6
	O = 7.8 (12.2)	S = 22.6 (28.6)	Cr = 24.5	—	—
	F = 9.2	Cl = 22.7		Br = 28.1	I = 36.6

observations on the compounds of phosphorus and sulphur appear to me to be conclusive on this point. It may turn out that the particular value to be assigned to carbon, for example, in the aromatic compounds is slightly different from that which it is found to possess in the fatty acids or the corresponding alcohols and ethers, but there is no question as to the quantivalence of the carbon in these several groups of compounds.

In concluding, I would express my conviction that far too little attention has hitherto been paid to the aid which a knowledge of the specific volume of a body may give towards elucidating its chemical constitution. The chemical history of a substance cannot now be held to be complete until the law of its expansion by heat between the limits at which it is ordinarily a liquid has been ascertained. A simple determination of specific gravity at some indefinite temperature is of no particular value in characterising a body; but the fact may become of great importance if there be added to it the knowledge of the thermal expansion of the substance. We have not to seek far for arguments to support this assertion. The extraordinary multiplication of isomerides which we have witnessed during the last few years demands that the various physical clues to chemical constitution, which are in our possession, should be more closely followed up than they have hitherto been. The mathematical investigations of Professor Cayley have made us familiar with the fact that the number of possible members of one group alone—that of the hydrocarbons of the C_nH_{2n+2} series—almost borders on the infinite; and it seems hopeless to expect that we shall have any other means of identifying, say, the eighteen different bodies of the formula C_8H_{18} which are theoretically possible, than are afforded to us by differences in their physical characters. Of course the knowledge of the specific volume is only one of the many physical exponents of the constitution of a body that we might have, and it may, of course, happen at times that the information this particular value conveys may not be of great moment, but in the present state of the question, when it is especially important to accumulate facts, the accurate determination of the various data upon which the estimation of this constant depends must ultimately prove of the greatest service.

XXII.—*Contributions to the History of the Orcins. Betorcinol and some of its Derivatives.*

By JOHN STENHOUSE, LL.D., F.R.S., and CHARLES E. GROVES.

ABOUT 32 years ago (Stenhouse, *Annalen*, 68, 104), in the course of an extended examination of the lichens with regard to the organic compounds contained in them, and derivatives of these compounds, a quantity of usnic acid obtained from the *Usnea barbata* and *Cladonia rangiferina* was submitted to destructive distillation. The distillate was found to contain a crystalline substance of the composition $C_8H_{10}O_2$, homologous with "orcin," and very closely resembling it in most of its properties. This new member of the orcinol group was named " β -orcin" from this circumstance, and as it was known that the erythrin and lecanoric acid from the *Rocella fuciformis* and the *Lecanoras* yielded orcinol, it was somewhat hastily inferred that the usnic acid in the *Usnea* and *Cladonia* was the source of the so-called β -orcin. Subsequent attempts to prepare the β -orcin by the distillation of pure usnic acid obtained from *Usnea barbata* yielded negative results; not a trace of the orcinol could be detected. This has been confirmed by other observers.

As there were not only many points of interest connected with this higher homologue of orcinol, but also great uncertainty as to what was the real source of the compound, we obtained a quantity of *Usnea barbata** from the same locality as that which had yielded the original specimen, namely, Roxburghshire (Scotland), and also—through the kindness of our friend Dr. James Young—from Durris, in Kincardineshire. The crude usnic acid extracted from the *Usnea*, which had previously been most carefully freed from every trace of *Evernia* or other lichen, was submitted to destructive distillation, and the distillate examined for the orcinol by means of chloride of lime solution. The crimson-red coloration produced at once showed that the *Usnea* from both localities contained the orcinol-yielding compound. It remained to be determined whether this was the usnic acid, or some other principle accompanying it in the lichen. Destructive distillation of carefully purified usnic acid from the samples of lichen from the two localities at once settled this point; not a trace of β -orcin could be discovered in the distillate. The results of these experiments, therefore, have definitely established that the usnic acid is not

* These lichens were kindly examined for us by Mr. Carruthers, of the British Museum, and also by Sir Joseph Hooker of Kew, both of whom pronounced them to be *Usnea barbata*.

the source from which the β -orcin is derived, but another substance accompanying it in the lichen in the same manner that evernic acid accompanies usnic acid in *Evernia prunastri*.

Betorcinol.

As the prefix α - or β - is now almost universally used to distinguish isomerides, it has been thought advisable to change the name " β -orcin" into betorcinol, so as to bring it more into harmony with the nomenclature employed at the present time.

In preparing betorcinol, $C_8H_{10}O_2$ or $C_8H_7Me_2(OH)_2$, the *Usnea barbata* is first most carefully picked over by hand, so as to free it from every particle of *Evernia* or other lichen which may be present, and is then steeped in 20 parts of water for 16 hours, in order to thoroughly soften and moisten it. One-tenth part of lime, equal to 10 per cent. of the original weight of the lichen, is slaked, and after being made into a cream with a sufficient quantity of water, is poured into the mixture, and the whole allowed to stand for an hour with occasional stirring. The partly exhausted lichen is then taken out, and treated in a precisely similar manner with 10 parts of water, and one-tenth part of lime for one hour, whilst the lime-extract is being filtered, which is most conveniently done through a bag-filter, with a pressure of 6 or 8 feet of the liquid. The lichen acids are precipitated from the clear solution as soon as possible, by gently acidifying with hydrochloric acid, collected, and washed with a little cold water. In order to completely exhaust the lichens, it is necessary to treat them four times with lime and water, but the quantity of both employed in the last two extractions may advantageously be diminished by one-fourth. The yield of dry crude lichen acids obtained from the specimens of *Usnea* examined, gathered in September and October, varied from 3 to $3\frac{1}{2}$ per cent.

The crude product, which consists chiefly of usnic acid mixed with but a very small proportion of the acid which yields betorcinol, is boiled with its own weight of lime and 40 parts of water for 3—4 hours. It is not necessary, in fact it is far better not to dry the acids before boiling them with lime and water; the amount of lime and water required can be easily reckoned for the quantity of usnic acid taken when the yield of crude acid which the particular sample of lichen gives has once been ascertained. By this mode of treatment the whole of the usnic acid is converted into the insoluble basic calcium compound described in a former paper (*Proc. Roy. Soc.*, **18**, 223, and *Annalen*, **155**, 51), whilst the other lichen acid splits up, yielding carbonic anhydride and betorcinol, the former combining with the lime to form calcium carbonate, whilst the betorcinol remains dissolved. As

the latter oxidises with the greatest readiness in alkaline solutions, it is necessary that the operation should be conducted in a flask furnished with an upright condensing tube with a small opening at the top, the heat being so regulated that steam in small quantity issues continuously from the upper end. When the reaction is completed, the solution is at once filtered through a vacuum-filter into dilute hydrochloric acid in quantity just sufficient to neutralise the lime. If this precaution be not taken, loss of the orcinol will occur through oxidation. The feebly acid solution is rendered strongly acid with acetic acid, filtered from a small quantity of flocculent precipitates, and evaporated on the water-bath: as the evaporation proceeds, a black tar is gradually deposited, arising apparently from the oxidation of a product of the action of the lime on the usnic acid or on some substance present in the crude usnic acid. When the solution has been reduced to about one-eighth of its original bulk, it is filtered, and the evaporation of the clear solution is continued, whilst the black tar which separates may be exhausted with boiling water, and the filtrate reserved for subsequent treatment along with the washings of the crude betorcinol. When the solution becomes concentrated, the impure betorcinol separates in the crystalline state, being almost insoluble in the concentrated solution of calcium chloride, derived partly from the calcium chloride in the crude lichen acids, and partly from the neutralisation of the lime by hydrochloric acid. The crystals, which are mixed with more or less of the black tar previously mentioned, are collected, washed with a little water, and dried. As the washings contain betorcinol, they should be reserved, together with the solutions obtained by treating the tar with boiling water, and evaporated with fresh quantities of betorcinol solution; or they may be concentrated and the betorcinol extracted by agitation with ether. Instead of employing hydrochloric acid to neutralise the solution of betorcinol obtained by boiling the mixture of crude acids with lime and water, sulphuric acid may be used: in this case the solutions, after being concentrated by evaporation and filtered from the calcium sulphate, must be agitated with ether to extract the betorcinol. The process first described is, however, far to be preferred for the preparation of the orcinol, whilst the last mentioned is useful when very small quantities are operated on, as when it is desired to examine a lichen for the acid which yields betorcinol.

In order to purify the crude product, the dry betorcinol is boiled with 50 parts of benzene, and filtered hot from the brown insoluble portion, which is again treated with benzene until nothing more dissolves: the benzene solutions are then concentrated by distillation, and on cooling deposit the nearly pure betorcinol in pale brown crystals, which may be collected, washed with a little benzene, and dried.

A crystallisation or two from boiling water (4 parts) renders it quite pure, although the crystals still retain a brown tinge. The amount of betorcinol obtained from *Usnea barbata* in this way rarely exceeds 0.1 per cent. of the weight of the lichen.

The purified betorcinol was found to have the same melting point (163°) as the original specimen prepared 32 years ago, and to be identical with it in all its properties.

Betorcinol is distinguished from orcinol not only by its higher melting point and in being much less soluble in cold water, but also in its chemical reactions, especially with hypochlorites and with ammonia. Betorcinol gives a characteristic bright crimson coloration with hypochlorites, very different from the purplish-red obtained with orcinol. Its reaction with ferric chloride is also more marked, a green coloration being produced at first, which gradually becomes darker with formation of a flocculent precipitate. In contact with ammonia solution, betorcinol rapidly acquires a bright red colour on exposure to the air, whilst the corresponding orcinol solution is but slowly changed. Schwarz (*Ber.*, 13, 543) has recently shown that when orcinol is gently heated with dilute soda solution and a little chloroform, an orange-coloured solution is produced, which has a most brilliant green fluorescence when viewed by reflected light. We find, however, that betorcinol behaves very differently when treated in a similar manner, giving a deep red solution which is almost entirely destitute of fluorescent properties.

Chlorobetorcinols.

Tetrachlorobetorcinol, $C_8H_6Cl_4O_2$, or $C_6Me_2Cl_2(OC)_2$.—This compound may be prepared by the action of chlorine on the orcinol, taking care that the former is always kept in excess, as when a solution of betorcinol is added to chlorine hydrate. A mixture of the crystalline chlorine hydrate with water is first prepared by passing a current of chlorine with occasional agitation through water to which about one-fourth of crushed ice has been added: betorcinol is then dissolved in 50 parts of boiling water, and the cooled solution is gradually added to a portion of the chlorine hydrate mixture, leaving the latter in slight excess. This is most conveniently effected by first adding the betorcinol solution in very slight excess, which is easily ascertained, as the orange coloration disappears instantly on agitation as long as the chlorine is in excess, but becomes permanent when all the free chlorine has been removed. A little more chlorine hydrate is then added, and the almost colourless mixture allowed to stand for 12–20 hours, when colourless tetrachlorobetorcinol is deposited in the crystalline state. If sufficient chlorine hydrate has not been employed, the crystals will be coloured yellow more or less: any very great

excess of chlorine should be avoided, however, as it is apt to oxidise the chlororcinol and occasion loss.* The yield in successfully conducted operations is about 160—165 per cent. of the weight of the betorcinol originally taken. Attempts were also made to prepare the tetrachlorobetorcinol by the method which had been so successfully applied to the chlorination of orcinol and resorcinol, namely, the action of potassium chlorate and hydrochloric acid on the orcinol, but the results were not satisfactory: apparently the molecule of the betorcinol is completely broken up by the powerful oxidising action of the chlorine peroxide produced by the action of the hydrochloric acid on the chlorate.

The tetrachlorobetorcinol may easily be purified by one or two crystallisations from boiling light petroleum (16 parts). It forms large white prismatic crystals which melt at 109° , and are easily soluble in benzene and in ether, but insoluble in water. The chlorine was estimated in the substance dried in a vacuum, with the following result:—

0.262 gram of substance gave 0.544 gram of silver chloride.

	Theory.	Found.
Cl in $C_8H_6Cl_4O_2$	51.45	51.37

The action of excess of chlorine on betorcinol, therefore, gives rise to the tetrachlorinated derivative, $C_8H_6Cl_4O_2$.

Dichlorobetorcinol, $C_8H_6Cl_2O_2$, or $C_8H_6Me_2Cl_2(OH)_2$.—The tetrachlorinated derivative just described is readily acted on by reducing agents, 2 atoms of chlorine being displaced by hydrogen: the best agent for this purpose is a solution of hydriodic acid containing 15 per cent. of iodine. The finely powdered tetrachlorobetorcinol is added in small portions at a time to a boiling solution of hydriodic acid of the strength indicated and a small quantity of red phosphorus, in a flask furnished with reversed condenser: care should be taken that each portion of the tetrachloro-derivative is reduced before adding the next, which may be known by the disappearance of the yellow colour due to the liberated iodine, and any lumps that may form must be broken up. After all the tetrachlorobetorcinol has been added, the boiling is continued for a few minutes until the last portions are reduced, and the dichloro-compound assumes the appearance of a mass of slender colourless needles. It is then collected, washed with water, and dried. One or two crystallisations from light petroleum (50 parts) suffice to render it pure. It forms long colourless needles which melt at 142° , and are soluble in carbon bisulphide, benzene,

* We wish to direct particular attention to the use of chlorine hydrate as a chlorinating agent, especially in those cases where it is desirable that excess of chlorine should be constantly present during the reaction.

and ether. A chlorine determination was made of the substance dried in a vacuum.

0.199 gram of substance gave 0.276 gram of silver chloride.

	Theory.	Found.
Cl in $C_8H_6Cl_2O_2$	34.30	34.31

The result of the analysis corresponds almost exactly with that required for dichlorobetorcinol, $C_8H_6Cl_2O_2$.

Bromobetorcinols.

Tetrabromobetorcinol, $C_8H_6Br_4O_2$, or $C_6Me_2Br_2(OBr)_2$.—The tetrabrominated derivative may be prepared in a manner similar to that employed for converting orcinol into pentabromorecinol (*Proc. Roy. Soc.*, 20, 76, and *Annalen*, 163, 179) by adding a solution of the orcinol to bromine and water, taking care to keep the bromine in excess; the action, however, does not take place so readily with betorcinol as with orcinol itself. The most convenient method of conducting the operation is to place 5 parts of bromine and 100 of water in a stoppered bottle, and add a solution of 1 part of betorcinol in 50 of water in successive portions, with agitation between each addition, so that there may always be excess of bromine in the liquid. As soon as the reaction is completed, the whole is allowed to stand for a few minutes, and then violently agitated, when the bromobetorcinol will collect into a soft pasty mass, which becomes hard after a time. The solution of betorcinol should be made with boiling water and cooled rapidly just before being used, agitation being avoided as much as possible, otherwise the betorcinol is apt to crystallise out. The crude tetrabromobetorcinol is dissolved in carbon bisulphide—in which it is very soluble—a slight excess of bromine added, and the solution allowed to evaporate spontaneously in a loosely covered beaker. The large colourless prisms of the bromobetorcinol which form may readily be separated from the traces of brown resinous matter, and purified by crystallisation from boiling light petroleum. In this way, betorcinol yields about 320 per cent. of its weight of tetrabromobetorcinol.

Another and perhaps more convenient method of converting betorcinol into the tetrabrominated derivative is to treat it with bromine in carbon bisulphide solution. For this purpose a mixture of 5 parts of bromine and 30 parts by measure of carbon bisulphide are poured on to 1 part of betorcinol in fine powder, and gently heated in a flask furnished with condensing tube; the betorcinol gradually disappears, whilst torrents of hydrobromic acid are given off. As soon as the whole of the betorcinol is dissolved, the dark red-brown

solution containing dibromobetorcinol and excess of bromine is poured off from traces of black tar into a clean flask, and agitated with its own bulk of warm water, when the colour gradually becomes lighter or entirely disappears. In the latter case sufficient bromine has not been employed, and it is necessary to add more. The carbon bisulphide solution of the tetrabromobetorcinol separated from the supernatant liquid is concentrated by distillation and allowed to evaporate spontaneously, the crystals which form being purified in the manner formerly described. A very pure tetrabromobetorcinol may at once be obtained by acting on pure colourless dibromobetorcinol with bromine and water at a gentle heat, and crystallising the product from carbon bisulphide and light petroleum. It crystallises in large colourless prisms melting at 101° , and very similar in appearance to tetrachlorobetorcinol. It is very soluble in ether, benzene, and carbon bisulphide, less so in petroleum. The analysis of the substance dried in a vacuum gave the following results:—

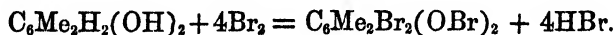
0.267 gram substance gave 0.442 gram silver bromide.

	Theory.	Found.
Br in $C_6H_6Br_4O_2$	70.48	70.44

Although the analyses left but little doubt that the compound obtained by the action of excess of bromine on betorcinol in presence of water was really the tetrabromo-derivative of the formula $C_6Me_2Br_2(OBr)_2$, it was considered advisable for the sake of confirmation to ascertain the amount of hydrobromic acid produced in the reaction. With this object two quantities of betorcinol of 0.2 gram each were treated with excess of bromine in presence of water, according to the method first described, and the amount of hydrobromic acid determined in the aqueous solution, after removal of the excess of bromine. The results were as follows:—

I.	II.	III.
0.4525 gram	0.4536 gram	0.4696 gram

In I, the excess of bromine was removed by exposing the liquid to a gentle heat in an open basin, until it had become colourless; whilst in II, the excess of bromine was removed by agitation with carbon bisulphide; III is the amount of hydrobromic acid which should be obtained theoretically from 0.2 gram of betorcinol, according to the equation—



Dibromobetorcinol, $C_6H_6Br_2O_2$, or $C_6Me_2Br_2(OH)_2$.—Like the tetrachlorinated derivative, tetrabromobetorcinol is readily acted on by hydriodic acid, even in the cold, dibromobetorcinol being formed; if,

however, the acid is concentrated, and the mixture is boiled for some time, the action goes farther, and betorcinol is regenerated. Some care is required, therefore, to convert the tetrabromo- into the dibromo-derivative, but even under the most favourable circumstances, the yield obtained falls far short of the theoretical. The finely powdered tetrabromobetorcinol is first treated in the cold with a little red phosphorus and a solution of hydriodic acid containing 12 per cent. of iodine; after 15—20 minutes, the dark brown mixture is heated in a water-bath at 60°, with occasional agitation, until the free iodine has been entirely reconverted into hydriodic acid by the action of the phosphorus, care being taken to break up any lumps of dibromobetorcinol that may be formed. Finally the whole is boiled for a minute or two to complete the reaction, and the nearly colourless dibromobetorcinol collected, washed thoroughly with cold water, and dried at a gentle heat. It may be purified by successive crystallisation from carbon bisulphide and light petroleum (100 parts).

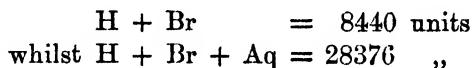
A far more productive and less troublesome process, however, is to treat the orcinol with bromine diluted with carbon bisulphide, for under these circumstances the action goes no further than the production of the dibrominated derivative, even when the bromine is in excess; the presence of water being necessary to convert the dibromo- into tetrabromo-betorcinol. A mixture of 8 parts of bromine, with 100 parts by measure of carbon bisulphide, is poured on to 3 parts of betorcinol in fine powder, and the mixture digested for some time in a flask furnished with a condensing tube; hydrobromic acid is given off, and the betorcinol gradually dissolves. After about thirty minutes' boiling, the carbon bisulphide solution becomes of a pale brown colour, and the reaction may be considered as completed. The digestion is then stopped, the clear solution poured off from the traces of dark coloured impurity adhering to the sides of the vessel, and the solution concentrated by distillation, until the dibromo-compound begins to crystallise out. When cold, the nearly colourless crystals are collected, and after being washed with a little cold carbon bisulphide, they are purified by crystallisation from light petroleum. The carbon bisulphide mother-liquors and washings, when distilled to dryness, yield a farther quantity of dibromobetorcinol, but it has a brown colour, and cannot be rendered colourless by simple crystallisation from any of its solvents; if, however, it is finely powdered and boiled for a minute or two with dilute hydriodic acid, the brown impurity is rendered insoluble in light petroleum, so that the bromobetorcinol may readily be obtained perfectly pure by one or two crystallisations from that solvent. It forms long needles, of melting point 155°, and closely resembles the corresponding chlorinated derivative in its relation to solvents. Dried in a vacuum—

0.219 gram substance gave 0.280 gram silver bromide.

	Theory.	Found.
Br in $C_6H_5Br_2O_2$	54.05	54.41

The percentage of bromine found indicates that the compound is dibromobetorcinol, $C_6H_5Br_2O_2$.

The fact that the action of bromine on betorcinol, when every trace of water is carefully excluded, only displaces two atoms of hydrogen in it, yielding a dibrominated derivative, whilst if water is present a tetrabrominated derivative is produced, is readily accounted for, if we take into consideration the great difference between the energy involved in the formation of gaseous hydrobromic acid by the union of bromine and hydrogen, and the formation of hydrobromic acid in aqueous solution; for, according to Thomsen (*Ber.*, 5, 770)—



In the betorcinol, the two hydrogen atoms, which are united with carbon in the benzene-nucleus, are comparatively easily displaced by bromine, so that the dibrominated derivative, $C_6Me_2Br_2(OH)_2$, is produced with evolution of gaseous hydrobromic acid. In the case of the two hydrogen-atoms united with oxygen in the OH groups, however, it is only when the much greater energy involved in the formation of hydrobromic acid in the presence of water is brought into operation, that displacement takes place with formation of the tetrabrominated derivative.

We have examined the behaviour of orcinol under the same conditions, and find that it is precisely similar to that of betorcinol, nothing but tribromorcinol being formed, unless water is present.

Iodobetorcinol.

Moniodobetorcinol, $C_6H_5IO_2$, or $C_6Me_2HI(OH)_2$.—This derivative may be prepared in a manner similar to moniodorcinol by the action of lead oxide on betorcinol and iodine in ethereal solution. The betorcinol is dissolved in 50 parts of dry ether, 2 parts of iodine are added, and as soon as it has completely dissolved, lead oxide in very fine powder is gradually added with constant agitation, until the solution is decolorised; the operation is most conveniently conducted in a stoppered bottle. The nearly colourless ethereal solution is separated from the lead iodide and excess of lead oxide, and after washing the residue with ether until nothing more is dissolved, the washings are added to the original solution, and the whole is distilled to dryness in the water-bath. The oily residue, which solidifies on standing, is boiled with

light petroleum; this dissolves all but a little brown matter, and on cooling, the impure moniodobetorcinol is deposited in the crystalline state. It may be purified by repeated crystallisation from light petroleum, when it melts at 93° . Iodobetorcinol is very soluble in ether, benzene, or carbon bisulphide, as is also the brown impurity which accompanies it. It is only very sparingly soluble in boiling water, more so in dilute spirit, but it does not crystallise well from the latter. The results of an iodine determination made on the substance, dried in a vacuum, were as follows:—

0.250 gram substance gave 0.222 gram silver iodide.

	Theory.	Found.
I in $C_8H_9IO_2$	48.11	47.99

This corresponds very closely with what is required by the formula $C_8H_9IO_2$.

Nitrosobetorcinol.

Mononitrosobetorcinol, $C_8H_9NO_3$, or $C_6Me_2H(NO)(OH)_2$, is readily prepared by the action of nitrosyl sulphate, $SO_2(NO).OH$, on betorcinol in aqueous solution; 2 parts of betorcinol is dissolved in 100 parts of boiling water, and the solution, after being filtered and cooled, is poured into a mixture of 7 parts of nitrosyl sulphate solution (*Journ. Chem. Soc.*, 1877, i, 545), containing 15 per cent. N_2O_5 , with 200 parts of water, when a brilliant, orange-red precipitate almost immediately makes its appearance. After allowing the mixture to stand for five minutes, the precipitate is collected on a vacuum filter, and washed by stirring it up with 100 parts of water, and again collecting; repeating the washing once more in the same manner, so as to remove the last traces of free acid, and finally drying at a gentle heat. The amount of nitrosobetorcinol obtained in this way is about equal to that of the betorcinol taken. Nitrosobetorcinol is moderately soluble in boiling water, and easily in alcohol, but it cannot readily be recovered in the crystalline state. It is very soluble in hot glacial acetic acid, and on cooling, separates in small bright red prismatic crystals. It is sparingly soluble in light petroleum and in carbon bisulphide, somewhat more so in hot benzene, crystallising out on cooling, and easily soluble in ether.

The attempts to prepare nitrobetorcinol, both from the nitroso-compound, and also by the direct action of nitric acid on betorcinol, gave unsatisfactory results, nothing but amorphous flocculent substances being obtained.

A nitrogen determination of nitrosobetorcinol gave the following results:—

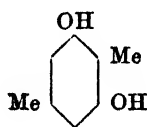
0.368 gram substance gave 24.6 c.c. nitrogen at 2°, and 770 mm. = 24.574 c.c. at 0°, and 760 mm. = 0.03083 gram of nitrogen.

	Theory.	Found.
N in $C_8H_8NO_3$	8.383	8.378

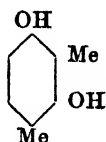
The numbers are identical with those required by the formula $C_8H_8(NO)O_2$.

It will be seen from these results, that in the action of nitrous acid on betorcinol, only one of the hydrogen atoms is displaced by the nitrosyl group, giving rise to mononitrosobetorcinol although resorcinol and orcinol under similar circumstances give dinitroso-derivatives. Considering that the action of nitrous acid on phenol—the *monhydroxy*-derivative of benzene—gives a *mononitrosophenol* in which the NO group occupies the para position with respect to the OH group, and that of the three *metadihydroxy*-derivatives of phenol, resorcinol and orcinol yield *dinitroso*-derivatives, whilst betorcinol yields only a *mononitroso*-derivative, it is not improbable that in the latter, the para position with respect to one of the OH groups is occupied by a CH_3 group.

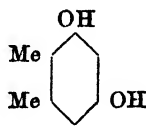
Of the four possible formulæ for betorcinol or dimethyldihydroxybenzene, I is capable of yielding a dinitroso-derivative, in which the NO groups can occupy a para position with respect to the OH groups, and in IV the para positions are occupied by CH_3 groups, so that it could not yield a nitroso-derivative of this class, whilst in II and III there is *only one* para position, in which the NO-group could enter, and consequently they would yield *mononitroso*-derivatives. Although our knowledge of the laws which govern the introduction of the nitrosyl group into the hydroxyl-derivatives of benzene is far too elementary to enable us to pronounce with certainty on this point, it seems more probable that the constitution of betorcinol is represented either by II or by III than by I or IV.



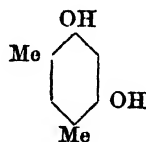
I.



II.



III.



IV.

The Acid which yields Betorcinol.

Barbatic Acid, $C_{10}H_{20}O_7$.—As the crude mixed acids obtained from the *Usnea* contain but a very small quantity of the acid which yields betorcinol in comparison with the usnic acid present, great difficulty was experienced at first in separating the two, and it was only after

many fruitless trials of fractional precipitation and crystallisation that a process was discovered which permitted the new acid to be isolated with certainty. The mixture of crude acids extracted from the *Usnea barbata* by lime in the manner described in the earlier part of this paper is collected, stirred up with water strongly acidified with hydrochloric acid, and allowed to stand for an hour or so; this treatment is necessary to completely decompose any lime salt of barbatic acid that may be present. The crude acids are then collected, washed, and dried at a gentle heat. After being powdered, 1 part of the mixed acids is digested with 40 parts of hot benzene, which dissolves all but a small quantity of dark-coloured mucilaginous matter. The filtered benzene solution is then distilled down to about one-sixth of its bulk, and the crystals which separate on cooling are collected and treated three times successively with ether, the first and second times in the cold, whilst the third time the acid is boiled for half an hour with the ether, and allowed to cool (using 10 parts of ether in all). The ethereal solutions, which contain all the barbatic and some usnic acid, are distilled to dryness, the residue treated in the cold with sufficient ether to dissolve the barbatic acid, and filtered from the residue of usnic acid, which is only sparingly soluble in cold ether; an equal bulk of benzene is then added to the clear ethereal solution, and the mixture is distilled down until all the ether has passed over, and also some of the benzene. On standing for some time, nearly pure barbatic acid is deposited in the crystalline state, whilst the small quantity of usnic acid present remains in the benzene solution.

When the benzene mother-liquor from which the first crop of mixed usnic and barbatic acids has separated is distilled with water to remove all the benzene, a brown crystalline mass is left, consisting principally of usnic, with some barbatic acid, the latter of which may be separated by treatment with ether, &c., in the manner just described.

The acid as thus obtained is usually slightly coloured, and contains traces of usnic acid, but it may be purified by crystallising it from benzene. Advantage may also be taken of the facility with which it forms a very sparingly soluble acid potassium salt. For this purpose, the nearly pure barbatic acid is dissolved in a slight excess of very dilute potash, and carbonic anhydride is passed into the solution; as soon as the excess of potash is saturated, a white curdy precipitate of the acid potassium compound of barbatic acid is produced. The passing of the carbonic anhydride must then at once be stopped, as otherwise any usnic acid which may be present will also be precipitated. The potassium compound after being collected and washed, is dissolved in cold water by the aid of a few drops of potash solution, and the clear liquid strongly acidified with hydrochloric acid. The pure bar-

batic acid may then be collected, washed, dried, and crystallised from benzene. It crystallises in colourless needles or long plates, and sometimes in short prisms; these melt at 186° , and at a somewhat higher temperature decompose with evolution of carbonic anhydride, and formation of betorcinol.

The acid dried at 100° was submitted to analysis, with the following results:—

I. 0.142 gram substance gave 0.330 gram carbonic anhydride, and 0.072 gram water.

II. 0.244 gram substance gave 0.567 gram carbonic anhydride, and 0.129 gram water.

	Theory.	I.	II.	Mean.
$C_{19} = 228$	63.33	63.38	63.38	63.38
$H_{20} = 20$	5.56	5.63	5.87	5.75
$O_7 = 112$	31.11	—	—	—
	<hr/> 360	<hr/> 100.00		

The analyses of this acid correspond with the formula $C_{19}H_{20}O_7$, which bears the same relation to betorcinol, $C_8H_{10}O_2$, that evernic acid, $C_{17}H_{16}O_7$, does to orcinol, $C_7H_8O_2$, and it is therefore not improbable that this acid is a dimethylevernic acid. As, however, this cannot be considered to be definitely established, we have provisionally named the new acid *barbatic acid*, from the circumstance that it exists along with usnic acid in the *Usnea barbata*. We have also examined *Cladonia rangiferina*, and find that it contains an acid which yields betorcinol when boiled with lime, and is in all probability identical with barbatic acid.

A short time ago Hesse (*Ber.*, 10, 1326) succeeded in obtaining an acid, which he termed "usnetic acid," (m. p. 172°) by treating an *Usnea* found on Calisaya bark with lime and dilute alcohol, and although this acid resembles barbatic acid in many of its properties, the much lower melting point, and the higher percentage of carbon (65.08) in the former renders it improbable that they are the same, especially as he states that his acid gave no sublimate when heated. It may be as well, however, to call attention to the well-known fact, that those lichen acids which may be regarded as derived from orcinol, such as lecanoric and evernic acids, yield ethereal salts with great readiness when boiled with alcohol, and that whilst we studiously avoided the use of alcohol in the preparation of barbatic acid, Hesse not only employed dilute alcohol and lime for the extraction of the mixed acids from the lichen, but purified his usnetic acid by dissolving it in hot dilute alcohol, and evaporating the solution.

XXIII.—On the Action of Organo-zinc Compounds on Quinones.
(Second Notice.)

By FRANCIS R. JAPP, M.A., Ph.D., Demonstrator in the Chemical
Research Laboratory, Science Schools, South Kensington.

Zinc-ethyl on Phenanthrene-quinone—(continued).

IN a previous communication (*Chem. Soc. J.*, 1879, 526) I described a compound of the formula, $C_{16}H_{14}O_2, C_2H_5O$, obtained by the action of zinc-ethyl on phenanthrene-quinone and subsequent decomposition of the product with alcohol. An attempt to prepare the compound, $C_{16}H_{14}O_2$, free from alcohol of crystallisation failed, but the mon-acetyl derivative, $C_{16}H_{13}O_2(C_2H_3O)$, was prepared and analysed.

The present paper describes the isolation of the compound $C_{12}H_{14}O_2$, and the study of some of its more important reactions. From the results thus obtained conclusions are drawn as to the constitution of this compound and of phenanthrene-quinone.

Isolation of the Compound $C_{16}H_{14}O_2$.

The expulsion of the molecule of alcohol of crystallisation from the compound $C_{16}H_{14}O_2, C_2H_5O$ was attended with some difficulty, due to the oxidisable nature of the substance. Heated in air the substance fused and became dark-coloured. Neither did heating in a current of carbonic anhydride lead to the desired result, analytical figures pointing to the presence of a mixture of $C_{16}H_{14}O_2$ with $C_{16}H_{14}O_2, C_2H_5O$ being obtained. As the fused substance evidently retained alcohol with great obstinacy, an attempt was made to desiccate the powdered crystals *in vacuo* over sulphuric acid, but the air which leaked into the receiver during the lengthened period required for desiccation caused the substance to become dark-coloured, and the analytical results were again unsatisfactory. An apparatus was therefore constructed in which the substance could be sealed up *in vacuo* over sulphuric acid. A small preparation tube (test-tube form) containing the substance was introduced into a long wide tube closed at one end. The long tube was then bent into the shape of the letter N, the tube with the substance remaining in the lower limb. At the point where the upper limb would terminate the tube was narrowed, and, sulphuric acid having been poured into the bend by means of a capillary funnel, the whole was exhausted thoroughly and sealed up. In this apparatus the substance was allowed to remain for some months, when an analysis showed that it had parted with its alcohol of crystallisation :—

I. 0.2095 gram of substance gave 0.6178 gram CO_2 and 0.1135 gram H_2O .

II. 0.1288 gram of substance gave 0.3782 gram CO_2 and 0.0705 gram H_2O .

	Calculated for $\text{C}_{16}\text{H}_{14}\text{O}_2$.		Found.	
			I.	II.
C_{16}	192	80.64	80.42	80.07
H_{14}	14	5.88	6.02	6.08
O_2	32	13.48	(13.56)	(13.85)
	238	100.00	100.00	100.00

The formula, $\text{C}_{16}\text{H}_{14}\text{O}_2, \text{C}_2\text{H}_6\text{O}$, on the other hand, would require C 76.06 and H 7.04 per cent.

The powdered substance had not changed in appearance, but it melted at 80° , the melting point having been raised 3° by the removal of the alcohol of crystallisation. By lengthened exposure to the air, it is transformed into a gummy mass, behaving in this respect like the compound $\text{C}_{16}\text{H}_{14}\text{O}_2, \text{C}_2\text{H}_6\text{O}$.

As it had thus been shown that the alcohol was present only in molecular combination, the crystallised compound, $\text{C}_{16}\text{H}_{14}\text{O}_2, \text{C}_2\text{H}_6\text{O}$, was employed in the following reactions instead of the compound $\text{C}_{16}\text{H}_{14}\text{O}_2$.

Oxidation.

Four grams of the crystallised compound were heated for a few minutes on a water-bath to expel a portion of the alcohol. The substance was then dissolved in glacial acetic acid, and a solution of 8 grams of chromic anhydride in the same solvent was gradually added. The temperature during the reaction was kept slightly below the boiling point of the acetic acid. On cooling, the liquid solidified to a mass of fine needles, which, after washing with water, possessed the bright orange colour of pure phenanthrene-quinone, and were soluble almost without residue in a concentrated solution of hydric sodic sulphite. The pure quinone, regenerated from the double compound with the acid sulphite, melted at 206° (m. p. of phenanthrene-quinone 205°). Analysis yielded the following results:—

0.1672 gram of substance gave 0.4928 gram CO_2 and 0.0595 gram H_2O .

	Calculated for $\text{C}_{14}\text{H}_8\text{O}_2$.		Found.
C_{14}	168	80.77	80.39
H_8	8	3.85	3.95
O_2	32	15.38	(15.66)
	208	100.00	100.00

Distillation with Zinc-dust.

A portion of the crystalline compound was distilled with ten times its weight of zinc-dust. As the distillate was of a dark colour and mixed with oily matters, it was re-distilled with zinc-dust. This time the distillate was of a faint yellow colour, and solidified perfectly on cooling. It was dissolved in hot alcohol, and an excess of an alcoholic solution of picric acid was added. On cooling, the liquid was filled with the characteristic long orange-yellow needles of the double compound of phenanthrene with picric acid, which, after recrystallising, melted at 143° , the melting point of phenanthrene picric acid. The hydrocarbon, after regeneration from the double compound, crystallised from hot alcohol in the rhombic plates characteristic of phenanthrene, and melted at $95-96^{\circ}$ (m. p. of phenanthrene 96°).

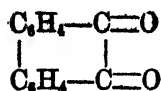
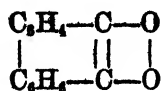
Behaviour with Caustic Alkali.

The crystalline compound dissolves in a solution of potassic hydrate, and from hot concentrated solutions the potassium salt crystallises on cooling in flat needles with a satiny lustre. This salt is very soluble in water, much less soluble in an excess of caustic alkali. When the solution is very concentrated, the excess of undissolved salt fuses in the liquid when heated, and floats on the surface like an oil. Exposed to the air the salt turns reddish-brown. Carbonic anhydride precipitates from the solution the compound $C_{16}H_{14}O_2$, which thus behaves like a phenol. When precipitated by acids, the compound, $C_{16}H_{14}O_2$, is obtained as an oil, solidifying with great difficulty, and then only partially. If, however, this oil is brought in contact with alcohol, it instantly solidifies superficially, owing to the formation of the crystalline compound, $C_{16}H_{14}O_2 \cdot C_2H_5O$, which is also obtained in the characteristic rectangular plates from the solution of the oil in hot alcohol.

The behaviour of the compound, $C_{16}H_{14}O_2$, when exposed to the continued action of an excess of boiling caustic potash, or when fused with caustic potash, has not been examined.

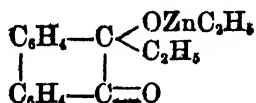
Theoretical Considerations.

There are two views at present held by chemists concerning the constitution of the quinones: that of Graebe, according to which the oxygen-atoms are attached by one bond each to two different atoms of carbon, whilst they are united to each other by the two remaining bonds; and that of Fittig, in which each atom of oxygen is attached by both its bonds to a separate atom of carbon. Applying these views to phenanthrene-quinone, we arrive at the following constitutional formulæ:—



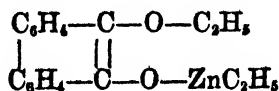
respectively employed by the above-mentioned chemists in their memoirs on phenanthrene (Fittig and Ostermayer, *Annalen*, 166, 361; Graebe, *ibid.*, 167, 131). According to Graebe's formula, the compound has the structure of a peroxide; according to Fittig it is a double ketone.

It seemed that the action of zinc-ethyl on such a compound might furnish a means of deciding between these opposing views. The action of zinc-ethyl on compounds in which oxygen is attached with both its bonds to one atom of carbon, has been studied. Judging from the analogy of known reactions, the action of zinc-ethyl on phenanthrene-quinone, supposing the latter to possess the constitution of a double ketone, ought to result in the formation of a compound of the constitutional formula—



in which, on decomposition with water, the zinc-monethyl group would be replaced by hydrogen, the resulting compound of the empirical formula $\text{C}_{16}\text{H}_{14}\text{O}_2$, having the double character of a tertiary alcohol and a ketone. The reaction might of course extend to the second CO-group.

The action of zinc-ethyl on a phenanthrene-quinone of the peroxide constitution was more difficult to predict, the case being without precedent. It seemed probable, however, that a separation of the bonds joining the two oxygen-atoms would take place, the two affinities thus liberated being satisfied by ethyl and zinc-monethyl respectively. The resulting compound—



would, on decomposition with water, yield phenanthrene-ethylhydroquinone, also of the empirical formula $\text{C}_{16}\text{H}_{14}\text{O}_2$.

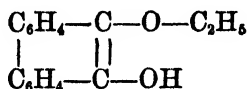
The empirical formula of the compound actually obtained is $\text{C}_{16}\text{H}_{14}\text{O}_2$, and it remains to be shown which of the above constitutional formulæ it possesses.

Both of the above compounds would contain one hydroxyl-group; consequently the formation of a mon-acetyl derivative as described in my first note (*loc. cit.*) affords no means of distinguishing between them.

Neither could the result of the oxidation be employed as a criterion. The second compound would yield phenanthrene-quinone, and it is probable that the first would act similarly, ethyl being separated from carbon in the process. Fittig (*Annalen*, 180, 27) has shown that a methyl group may thus be replaced by oxygen in the formation of oxyisoxylquinone by the oxidation of diamido-mesitylene.

The crucial test would be the total reduction of the substance to its parent hydrocarbon. The first compound ought, under these circumstances, to yield ethylphenanthrene; and the second, phenanthrene. It has just been shown that, in the distillation of the compound $C_{16}H_{14}O_2$ with zinc-dust, the product of the reaction is phenanthrene.

The ethyl group is therefore not attached directly to carbon; the compound has the constitution expressed by the formula—



and is *phenanthrene-ethylhydroquinone*. This view is supported by its behaviour towards caustic alkalis, with which it forms phenylates. The phenylic hydroxyl is attached to the central nucleus of phenanthrene (*Chem. Soc. J.*, 1880, 37, 88).

The formation of such a compound follows naturally from the peroxide constitution of phenanthrene-quinone, but could not be explained, on the supposition of double ketonic structure, without the further hypothesis of an intramolecular change.

It seemed, moreover, that, if phenanthrene-quinone is a peroxide, it ought to possess oxidising properties. For example, it might unite directly with an aldehyde to form the hydroquinone ether of the corresponding acid. Thus phenanthrene-quinone and benzoic aldehyde might yield phenanthrene-benzoylhydroquinone. To test this, phenanthrene-quinone and benzoic aldehyde were heated for several hours in a sealed tube to 250° . The reaction did not take place exactly in the sense contemplated, but free benzoic acid was formed in large quantity together with a complicated benzoyl derivative of phenanthrene. As no benzoic acid could be obtained at lower temperatures, it would perhaps be rash to ascribe its formation to a direct oxidation. I am at present engaged, in conjunction with Mr. Edgar Wilcock, in studying the action of aldehydes on quinones. The reaction has already yielded interesting results, which we hope soon to be able to lay before the Society.

In this and in my former communication, I have described the application of the zinc-ethyl reaction to the study of an ortho-quinone, and the result seems to me to render it in the highest degree probable that we have to deal here with a substance of peroxide structure—

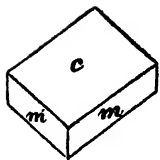
that in this case at least the view first suggested by Graebe is correct. It will be interesting to extend this reaction to the para-quinones—benzoquinones and α -naphtho-quinone. Undoubtedly the discovery that the oxygen-atoms in benzoquinone are in the position 1 : 4, has done much to shake the faith of chemists in Graebe's view. Both benzoquinone and naphthoquinone, however, possess the closest analogy in their properties to phenanthrene-quinone. Another point of interest will be the study in this direction of anthraquinone—a compound entirely *sui generis*, perhaps not a quinone at all.

XXIV.—On Pyrene.

By WATSON SMITH, F.C.S., F.I.C., Demonstrator and Assistant Lecturer on Chemistry in the Owens College, and GEORGE WM. DAVIES.

THE crude material for this investigation was obtained from Dr. T. Schuchardt, of Goerlitz, and consisted of a dark brown crystalline mass, almost in the condition of a powder. This was dissolved in light petroleum-spirit, and boiled for a long time with animal charcoal, filtered, and recrystallised. The crystals were then redissolved in fresh spirit, and a tolerably dilute solution was formed which was allowed to stand for two months, when crystals were obtained in well-defined monoclinic prismatic tables, showing uneven base-faces. The colour of the crystals was still a light yellow.

These crystals melted at 149° C. The most perfectly formed of them were now picked out and placed in the mother-liquor from the previous crystallisation, when, after about six weeks, three or four splendidly formed specimens were obtained. The best of these we sent to Professor Groth, of Strassburg, who kindly offered to make an examination of it for us. We give his report verbatim:—"This (crystal) is, as a specimen, splendidly formed, but unfortunately contains too few faces to render it possible completely to estimate the axis-relationship. Several years ago I received some small crystals of pyrene from Fittig's laboratory, which Herr Hintz had prepared, and described in his dissertation. These exhibited exactly the same form, viz., a monosymmetric combination of $c = (001)$ base, and $m = (110)$ prism—



$$mm = (110)(\bar{1}\bar{1}0) = 111^\circ 16'$$

$$mc = (110)(001) = 84^\circ 0'.$$

With your crystal one of my pupils, Mr. Shadwell, found—

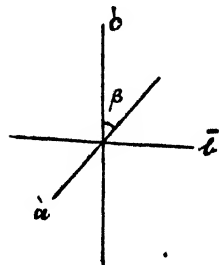
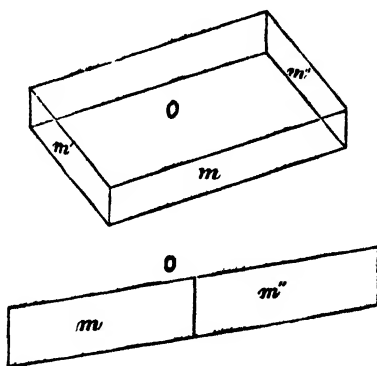
$$mm = (110)(\bar{1}\bar{1}0) = 109^\circ \text{ approx.}$$

$$mc = (110)(001) = 84^\circ \text{ ,,}$$

Since the surfaces in both cases were very curved and uneven, the identity of the substance is established with absolute certainty, only the so much desired completed development is not attained."

It is now our intention to attempt the preparation of a completely developed crystalline form of this hydrocarbon, or at least one with increased facial development, so as to render more easily observable the measurement of the vertical axis.

We enclosed another crystal to Dr. Chas. O. Trechmann, of Hartlepool, who kindly undertook its estimation also. This crystal might have been somewhat better developed than the one sent to Professor Groth for the purposes of measurement. Dr. Trechmann's observations, as will be observed, agree remarkably well with those of Groth, and he (Trechmann) has been able to go further. We subjoin his report:—



$$\begin{aligned} o &= 0P (001) \\ m &= \infty P (110) \\ a &: \bar{b} : \bar{c} \\ 1.498 &: 1 : p \\ \beta &= 79^\circ 25' \end{aligned}$$

"The angles can only claim to be approximations to the truth, for the crystal was rather large for measurement, and the irregular surfaces gave multiple reflexes. Nevertheless, until more perfect material is examined, my numbers will amply suffice. Of the system there is no doubt, as in the Nörremberg polariscope I saw both optic axes in the field of view. More exact determinations of optical properties are precluded on account of the crystal not being clear."

Hydrocarbon Pyrene, C₁₆H₁₀.

System : Monoclinic—

Forms : 0P(001) O

 ∞ P(110) m

Measured angles (interfacial).

 ∞ P : ∞ P (over ∞ P ∞)..... 68° 21' ∞ P : 0P 95 55½.*Elements.*— $a : b : c$

1.498 : 1 : ?

Cleavages : prismatic, parallel *m* imperfect, pinacoidal, parallel *o* perfect. Optic axes visible in 0P by means of Nörremberg; angle therefore small. Plane of optic axes normal to plane of symmetry. Acute bisectrix approximately normal to 0P.

A combination of the substance was next made, and the results obtained were as follows:—

Weight of substance taken = 0.303 gram.

This yielded 0.1445 gram H₂O and 1.0525 gram CO₂.

Hence—

	Found.	Calculated for C ₁₆ H ₁₀ .
	p.c.	p.c.
Carbon.....	94.73	95.05
Hydrogen	5.28	4.95
	<hr/> 100.11	<hr/> 100.00

Two vapour-density determinations were made by Victor Meyer's method, using the lead-bath, and vaporising the substance in an atmosphere of nitrogen. The following results were obtained:—

Calculated Vapour-Density of Pyrene = 6.999 (assuming the Molecule as C₁₆H₁₀).

EXPERIMENT I:—

B = 770.05

w = 13.365*t* = 16°

S = 0.0705 gram

V = 8.4 c.c.

and employing Meyer's formula $d =$

$$\frac{S(1 + 0.003665t)587780}{(B - w)V}$$

where B = height of barometric column at 0°,

w = tension of aqueous vapour for *t*,*t* = temperature of the air in graduated tube,

S = weight of substance taken,

V = vol. in c.c. of displaced nitrogen,

d = vapour-density.

EXPERIMENT II:—

B = 776.75

w = 11.906*t* = 14°

S = 0.0685 gram

V = 8 c.c.

$$(I.) d = \frac{0.0705(1 + 0.003665 \times 16)587780.0}{(770.05 - 13.635)84.} = 6.904$$

$$(II.) d = \frac{0.0685(1 + 0.003665 \times 14)587780.0}{(776.75 - 11.906)8.} = 6.920$$

Vapour-Density of Pyrene (C₁₆H₁₀).

	Found.	Calculated.
(1.)....	6.904	6.999
(2.)....	6.920	—

Mean .. = 6.912

We found, in using the lead-bath, it was best to cover the part of V. Meyer's apparatus dipping beneath the lead in the bath with lamp black. This was effected by simply smoking it well over a luminous gas flame. The glass is thus much less liable to crack, and furthermore the lead, which otherwise adheres to it more or less persistently, does not now do so. On wiping the apparatus from the lamp black, it becomes perfectly clean and bright, and is absolutely free from adhering lead.

XXV.—Analyses of the Ash of the Wood of Two Varieties of the *Eucalyptus*.

By WATSON SMITH, F.C.S., F.I.C., Demonstrator and Assistant Lecturer in the Owens College, Manchester.

THE samples of the wood of *Eucalyptus rostrata* and *E. globulus* were kindly supplied to me by Jas. Young, Esq., LL.D., F.R.S., who had also suggested to me previously that I should make an examination of their properties and the composition of their ashes. The common or popular names of the varieties mentioned are the *red* and *blue gum trees*. The pieces of wood I received appeared to be stout branch or crop wood, and had the bark still on them. They were about 7 inches long, and 2 to 2½ inches in diameter. The wood of the "red gum" variety (*E. rostrata*) was evidently closer and denser in texture, and the bark was thinner and smoother than with the wood of the "blue gum" variety. In the latter the bark was both rougher, coarser, and thicker. I took samples of the wood to an experienced Swiss wood worker in Zürich, and requested him to plane them down to thin shavings, with the exception of a tranverse section of each variety to be reserved for specific gravity determinations. I requested him also to notice carefully any peculiarities he might observe

in the wood, and report them, with his opinion of the quality. Calling subsequently, I noticed at once on entering the workshop, a rather large one, the odour of the essential oil peculiar to *Eucalyptus*. The atmosphere of the whole shop was fragrant with it. On planing the wood to shavings, the odour is rapidly diffused abroad. The joiner expressed astonishment at the extreme hardness of the wood, which had quite turned the edge of his plane. The wood of the "red gum" or *E. rostrata* was considerably the harder of the two. The timber of such a tree, he said, must be of very great value. The wood of the *blue gum* was rather behind the other in point of hardness and solidity.

Determinations were now made of the specific gravity of these woods, in what may be termed the "air-dried" condition. The sections of both varieties had been placed in a dry atmosphere for one month. The results were as follows:—

	"Red gum," or <i>E. rostrata</i> .	Blue gum, or <i>E. globulus</i> .
Sp. gr. =	0·8112	0·752

The sections were now planed down to thin shavings (bark included), and these were burnt in a platinum dish to a white ash, which was weighed. The percentages of ash obtained were—

	<i>E. rostrata</i> .	<i>E. globulus</i> .
Ash	2·25 p.c.	2·01 p.c.

Analyses of the ash obtained by burning the shavings obtained from the larger samples gave the following numbers:—

The ash was white, inclined to straw colour.

	<i>E. rostrata</i> . p.c.	<i>E. globulus</i> . p.c.
K ₂ O	9·50 }	25·00
Na ₂ O	3·40 }	
MgO	6·30	6·47
CaO	43·80	35·08
Ferric and aluminic } phosphates }	0·78	1·07
MnO	trace	trace
Al ₂ O ₃	—	trace
SiO ₂	0·29	0·34
SO ₃	1·57	1·55
Cl	0·60	0·85
Sand and carbon	1·77	1·04
CO ₂	31·28	29·33
	<hr/> 99·29	<hr/> 100·73

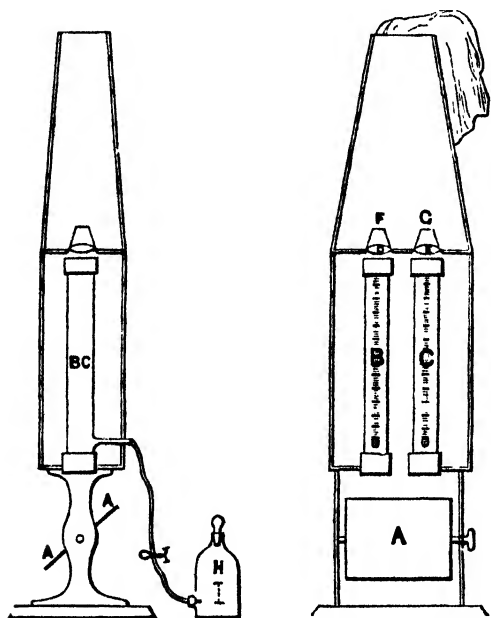
I made a few experiments with a large quantity of the leaves of *E. globulus* procured in Italy, and found that on steaming them, when the essential oil readily passes over with the steam and condenses, a dark brown liquor remains containing considerable quantities of tannin. I believe from the considerable quantity of tannin present in the leaves they may yet be turned to profitable account. The simple decoction with hot water has a fragrant odour, and a by no means unpalatable flavour. I was informed that in some parts such a decoction is prepared and drunk like tea.

XXVI.—*On the Reflection from Copper and on the Colorimetric Estimation of Copper by means of the Reflection Cuprimeter.*

By THOMAS BAYLEY.

THE author has shown (*Phil. Mag.*, March, 1878) that a remarkable relation exists between the light reflected from metallic copper and that transmitted by solutions of its salts. The light reflected from the surface of the metal contains all the elements of white light, but the region of the spectrum to the red side of the D line is more intense than in the spectrum of the reflection from a white surface of equal illumination, and lengthened out for a short distance beyond the point where the visibility of the ordinary spectrum ceases. The light transmitted by dilute solutions of cupric salts is deficient in those rays which the spectrum of reflection has in excess, and the space below the sodium line is dark. It follows then that if we look at a copper surface through a sufficient thickness of cupric sulphate solution, the metal appears silver-white, for the solution absorbs the excessive rays which make the copper red. Upon these facts the construction of the reflection cuprimeter is based. The instrument (as made by Messrs. Jackson, 65, Barbican) is shown in the accompanying figure: it is a mirror of copper supported upon a horizontal axis, and capable of rotation. The direct light from the sky is reflected from this surface vertically upwards through two tubes B and C, closed at the bottom by plates of glass, and protected from extraneous light by a wooden case. The sheaves of light passing up the tubes are concentrated by the convex lenses D and E upon the semi-transparent discs F and G, composed of two or three layers of white tissue paper moistened with glycerin. Surmounting the case containing the lenses and tubes is a

conical box blackened inside, which screens the discs and the eye of the operator from foreign light. The glass tubes are fitted at their lower extremities with side tubes which communicate by caoutchouc piping with the aspirators H and I. The right-hand tube contains a



Side elevation.

Front elevation.

Scale 2 meters to 1 foot.

standard solution of copper; in the other is placed the solution under examination, and the level of the liquid in either tube can be regulated by means of the aspirator. The standard solution is made by dissolving 1 gram of pure copper in nitric acid, adding a slight excess of sulphurous acid, and diluting to a liter at 15° C. The depth of this solution required to produce a white disc was determined in the following manner:—The surface of half the mirror was replaced by silver, so that the silver reflection passed through one tube and the copper reflection through the other. The former tube contained distilled water, the standard-copper-solution was placed in the latter, and its depth adjusted until both discs were equally white. In operating for this purpose, it is best to make four determinations, starting with the column alternately too long and too short; the errors then have a tendency to be alternately positive and negative, and the mean of the series is very near to the true result. Whatever the tint of the disc over the varying column, the eye invests the white disc with the complementary colour, but when the blue liquid exactly neutralises the

reflection from the copper both discs are white. In these preliminary experiments the tubes were graduated in centimeters, and the means of three series of experiments of six each were 8·00, 8·01, and 8·03; we may therefore take the length of the column of standard solution required to balance the reflection from the plate as 8·01 cm. The density of a solution of copper containing 1 gram per liter, after correcting for the acid, is not far from that of distilled water, so that the liquid contains approximately ·1 per cent. of the metal. Optically such a liquid may be considered as copper diluted and freed from the conditions which fetter it in the state of solidity. Solid copper is coloured because it decomposes part of the incident white light, reflecting the red rays and suppressing the remainder; but that this remainder penetrates a minute distance into the metal we know from the experiments of Faraday, who showed that thin films transmit bluish light. In the dilute solution the molecules are emancipated from the conditions which produce opacity. Since the length of the column required to produce white light is inversely as the quantity of copper present, and since a solution of copper containing ·1 per cent. required a length of 8·01 cm., a solution of copper containing 100 per cent. of metal, that is to say pure copper, would require a thickness of ·0801 mm., supposing its molecular condition to remain unaltered. We thus arrive at an abstract conception of copper derived from the ordinary conditions of solidity, existing as a transparent substance transmitting blue light.

The length ·0801 mm., which we may call a "cuper," is conveniently used as the basis of the graduation of the cuprimer. The standard solution requires a thickness of 1,000 cupers to produce a white disc, and represents copper 1,000 times diluted. A solution containing half this quantity of copper requires a thickness of 2,000 cupers and represents copper 2,000 times diluted. In general if c equals the number of cupers expressing the thickness of the solution when the disc is white,

c = vol. of liquid (in cubic centimeters) which contains 1 gram of copper, .

and $\frac{1,000}{c}$ = amount of copper in grams contained in one liter of solution.

The following, which are the results of an actual series of observations, indicate the degree of accuracy possible with the instrument. The solution contained ·801 gram of copper per liter.

True reading.	Observed readings.	Corresponding to copper per liter.
1248	1240	0·806 gram
	1230	0·813 „
	1250	0·800 „
	1260	0·793 „
	1260	0·793 „
	1230	0·813 „
	<hr/>	<hr/>
Mean	1245	Mean.. 0·803 „

Iron in considerable quantity is not injurious, if it is reduced to the ferrous condition. A solution containing 1 gram of iron and ·5 gram of copper per liter gave the following readings:—

1980
1970
2000
2000
2010
2020

In estimating the copper in an ore, or in brass, such a quantity as is supposed to contain about 1 gram of copper is dissolved in nitric acid, treated with excess of sulphurous acid, boiled, cooled, and made up to a liter. The solution is then observed in the instrument. The plate must be uniformly polished, and quite free from tarnish. It might, of course, be possible to dispense with the standard solution and balance the unknown solution against a plate of silver; but although under these circumstances the two discs are white, they are not equally illuminated, as it would seem, for the following reasons:—A silver plate reflects a certain quantity of white light; an equally polished copper plate reflects the same amount of light, minus that abstracted from the portion corresponding with the red residuum. This residuum being absorbed by the solution, it follows that the reflection from the copper is less intense than the silver reflection by the amount of light thus disposed of by transmission and absorption.

The frosted surface of copper produced by electrodeposition has conditions of reflection differing widely from that of polished surfaces. Such a surface reflects a larger quantity of red light, and requires a much greater thickness of copper solution to neutralise it. It is possible, however, that the white light reflected is greater in equal proportion, for the surface thus neutralised has the brilliant appearance of pure white paper. I hope to return to this subject in a future communication. It is worthy of remark in passing that the same relation seems to exist between the hydrated oxides of copper as between the metal and

its solutions. The hydrated suboxide (Cu_2O) seen through a strong solution of copper has a dead black appearance. Its reflection consists principally of red rays, and it therefore appears black when these are absorbed. The hydrated oxide (CuO) has more or less the colour of cupric solutions. It may be observed that the same relations exist between certain salts of nickel and cobalt, which, when mixed together, yield a colourless grey powder or a colourless solution.

XXVII.—*Note on the Products of Combustion of Coal Gas.*

By LEWIS T. WRIGHT.

SOME years ago I attempted to convert the sulphur in coal gas into sulphuric acid by burning the gas in a Bunsen burner in an atmosphere charged with the nitrogen oxides evolved from fuming nitric acid, but in no case did I succeed in obtaining more than 60 per cent. of the sulphur in the form of sulphuric acid. I was much struck with the powerful odour and flavour of the products of combustion at the outlet of the apparatus, which were suggestive of ozone, though more pleasant and aromatic.

I also drew the products of combustion of coal gas burning in a normal atmosphere through several wash-bottles charged with distilled water. With gas containing 17 grains of sulphur per 100 cubic feet I obtained only sulphuric acid equal to 2 or 3 grains of sulphur per 100 cubic feet.

Believing that sulphur on combination left the flame in the form of SO_2 , and that the small amount of H_2SO_4 found in the wash-bottles was due to the partial oxidation of the sulphurous acid dissolved in the water, I conceived the idea of making a quantitative test by drawing the products of combustion through solutions of iodine of known strength. My expectations were not at first realised, for the results obtained were low. I should have, perhaps, attributed these low results to the formation of sulphuric acid before the products of combustion reached the iodine-solution, had I not noticed that a reappearance of free iodine in some of the wash-bottles after the iodine-solution had been completely bleached and the current of gases stopped. I satisfied myself by means of starch that the reproduced yellow colour was due to iodine. After removing all free iodine by sodium thio-sulphate, a reappearance of iodine was noticed when the solution had been standing by for some time. The quantity of sulphurous acid was so very much within the safe limit given by Bunsen, that I was

not disposed to believe that the reproduction of iodine was due to the converse reaction—



but attributed it to the disturbing influence of nitrous acid which is always formed during the combustion of coal gas in ordinary air. The iodine-solution contained iodide of potassium, as is usual. To whatever cause the reappearance of the iodine may be due, it was found to be prevented by the use of pure sodium bicarbonate in the iodine-solutions, and it was found that with this precaution the sulphur of coal gas could be estimated by burning so small a quantity as half a cubic foot. I am therefore inclined to believe that sulphurous, not sulphuric, acid is produced by burning coal gas.

In 1877 I conducted some experiments by which it was proved that nitrous acid was produced by the combustion of coal gas in ordinary air, that the amount was increased by charging the air with ammonia vapour, and that when a special process was employed to remove ammonia compounds both from the air and coal gas used, no nitrous acid could be detected, and that the iodide paper did not discolour. During the first attempts at the air-purification, the futility of the ordinary methods of washing by bubbling through solutions was evident. Theoretically it is impossible to remove one gas entirely from another by washing bubbles of the gas, and I find that in drawing the products of combustion rather rapidly through eight wash-bottles traces of sulphurous acid appear in the last bottle.

I never had the least difficulty in obtaining the blue reaction when paper moistened with potassium iodide and starch has been exposed to the gases flowing out of an apparatus under which coal gas is burning in a Bunsen burner. Since reading the reports of Mr. Ridout's paper on the production of ozone, &c., I have made the following experiments in the hope that the cause of the blue reaction might be made clear.

The apparatus first employed was a trumpet-shaped tube bent at a right angle and connected to a long glass tube bending upwards at an angle of about 45°. Under the trumpet-tube was placed a laboratory Bunsen burner with a flame of coal gas consuming about 1 foot per hour. The effluent gases were tested with bibulous papers of five kinds, and the following reactions were obtained in about 15 minutes:—

- | | |
|--|--------------------|
| (1.) Iodide and starch paper..... | Blue coloration. |
| (2.) Indigo paper..... | Bleached. |
| (3.) Naphthylamine hydrochlorate | Violet coloration. |
| (4.) Griess' reagent (metaphenylene diamine) | Orange „ |
| (5.) Sulphide of lead paper | Bleached. |

I then tried the same papers on the effluent gases from the well-known gas-referee's sulphur-apparatus, but had previously moistened the glass marbles with pure potash-solution. The papers were coloured or bleached as before. As a final experiment, the products of combustion, before passing into the air, were made to traverse a long horizontally placed glass tube kept red-hot by two powerful Bunsen burners. On testing the effluent gases as before the same reactions were observed.

I find that a consumption of coal gas in a Bunsen burner, equal to .05 cubic foot, is sufficient to produce the above reaction when ordinary air is employed, but that when the air is purposely contaminated with ammonia .01 to .02 cubic foot suffices.

Referring to a former paper (*Chem. Soc. J.*, 1879, 35, 42) it will be found that I was able, by a special method of purification, to avoid the formation of any body in the products of combustion acting upon iodide of potassium.

To sum up, I will state my opinion that ozone is not formed by the combustion of coal gas, for it would be destroyed by sulphurous and nitrous acids, which are undoubtedly formed; and it is significant that the reaction with iodide paper does not appear when ammonia or its compounds are removed from the air employed for combustion.

XXVIII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

No. V. "*Note on Chemical Equilibrium.*"

By M. M. PATTISON MUIR, M.A., F.R.S.E.

1. THE influences exerted by changes in the conditions of certain chemical actions on the course of these actions has been considered in former papers. The conclusions therein arrived at are, I think, capable of wide application. In the present note I wish to glance at some of these applications, and to illustrate them by references to one or two special instances of chemical change.*

* The subject of the accelerating action of foreign bodies on a chemical change has been treated of by Harcourt and Esson (this Journal, 20, 460). The equilibrium of heterogeneous substances has been mathematically and dynamically considered in a remarkable paper by Professor J. Willard Gibbs, of Yale College, a summary of which, in non-mathematical language, by Professor Clerk-Maxwell, is to be found in the South Kensington Science Conferences, 1876.

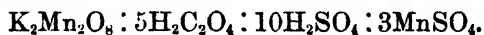
2. In their celebrated memoir (*Etudes sur les Affinités Chimiques*) Guldberg and Waage consider those chemical changes to be complete in which the final and initial collocations of matter are the same. They regard a chemical change as consisting of two parts, a direct and a reverse change; and they call those changes complete in which the latter is equal (and of course opposite) to the former.

But as a general rule a condition of stable equilibrium is attained before either part of the cycle has been completed. The attainment of this condition is dependent on the coefficients of affinity of the reacting bodies, the masses of these bodies, and the physical conditions under which the change proceeds. Hence the attainment of this condition may be prevented, broadly speaking, by variations in the physical conditions of the change, or by the calling into play of secondary forces which tend to produce new molecules or groups of molecules, the formation and existence of which, again, induce a chemical change or changes other than that which would have occurred had these molecules not been produced.

3. In the first and third of these "contributions" instances have been given in some detail of chemical changes, the course of each of which was shown to be modified by the inductive action of secondary changes, themselves brought about by variations in the physical circumstances of the reactions.

4. It occurred to me that by duly arranging the experimental conditions, the velocity of the change which occurs when potassium permanganate, oxalic, and sulphuric acids, are mixed, might be altered so that results should be obtained analogous to those noticed in the cases already referred to of bismuthous chloride, hydrochloric acid, and water; and barium chloride, potassium oxalate, and water.

The substances used were mixed in the proportions—



(See Harcourt and Esson, *loc. cit.*)

In the first series of experiments the permanganate solution was gently run from a burette into the mixture of the other compounds; after the expiry of a certain number of minutes the whole liquid was shaken up, and at the expiry of a second period of minutes the action was stopped by quickly adding a measure of potassium iodide solution. The free iodine was determined by a standard sodium thiosulphate solution.

In the second series of experiments the permanganate solution was run in quickly with constant shaking.

In both series the amount of $\text{K}_2\text{Mn}_2\text{O}_8$ used was 0.141 gram and the total liquid measured 200 c.c. The temperature varied from 14° to 17°.

Series I. Permanganate run in gently; liquid remained at rest for 3 minutes, then shaken up and action stopped after—

Minutes.	Total minutes of action.	Percentage of $K_2Mn_2O_8$ decomposed.	Mean.
0	3	56.0	56.0
3	6	67.0	67.0
5	8	72.0, 72.0	72.0
7	10	71.0, 71.0, 73.5, 78.5	73.5
9	12	78.5, 82.0	80.0
13	16	89.0, 87.0	88.0

Series II. Permanganate run in with constant stirring.

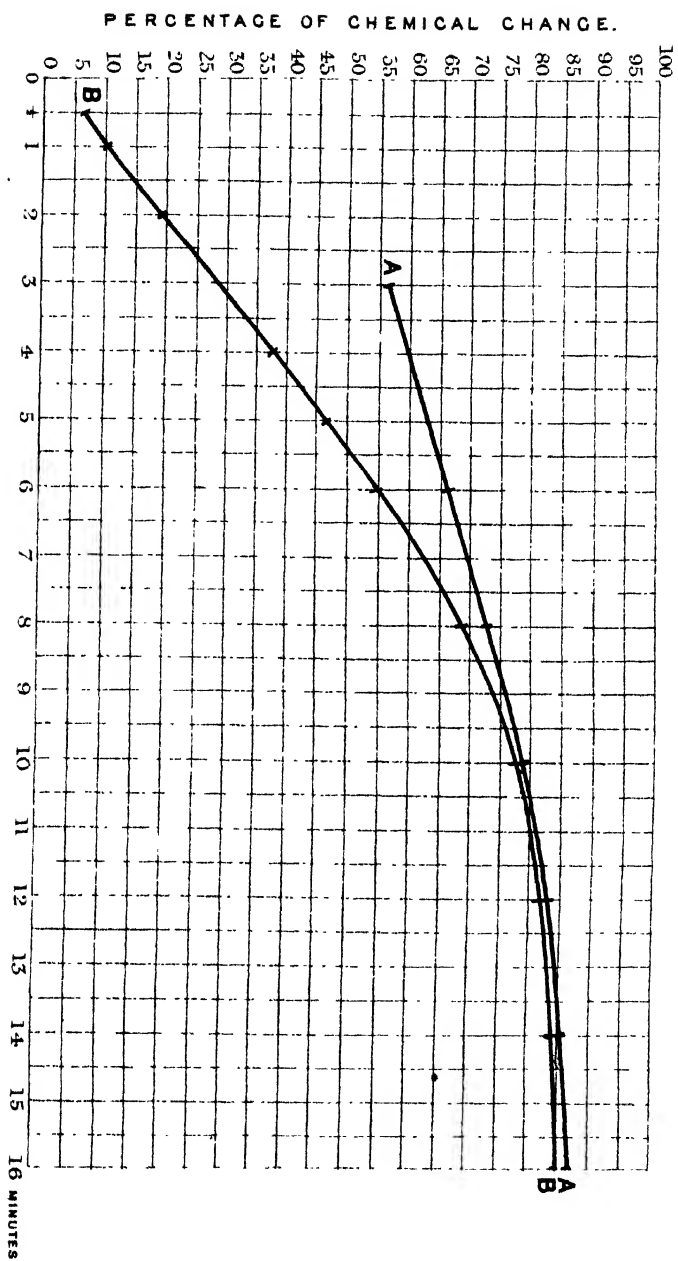
Action stopped after minutes.	Percentage of $K_2Mn_2O_8$ decomposed.	Mean.
$\frac{1}{2}$	6.0	6.0
1	10.0	10.0
2	17.5, 17.5	17.5
4	37.5	37.5
5	45.0	45.0
6	57.5, 52.5	55.0
8	70.0, 72.0, 69.0	70.0
10	76.0, 78.0	77.0
14	81.5, 82.5	82.0
16	84.5, 85.5	85.0

Curve A represents the results of Series I. Curve B those of Series II.

5. It is thus shown that during the earlier part of the reaction which occurs when potassium permanganate, oxalic acid, sulphuric acid, and manganous sulphate, are mixed, the velocity of the change varies in accordance with the manner of mixing the reacting bodies.

In the paper alluded to Harcourt and Esson analysed the reaction under consideration, and showed that it probably consists of four distinct changes. The numbers obtained by them were, however, they tell us, always consistent with the hypothesis that each of these changes, occurring simultaneously, obeys the law—"When any substance is undergoing a chemical change, of which no condition varies excepting the diminution of the changing substance, the amount of change occurring at any moment is directly proportional to the quantity of the substance."

In the modification of the reaction described above the conditions were arranged so that one of those changes into which the reaction may be divided had an advantage given it over the others, and hence the abnormal results of Series I.



6. Another instance of modification of a chemical change induced by variations in the physical conditions of that change, has been recently noticed by me. In attempting to dissolve a sample of very refractory hæmatite in sulphuric acid by the aid of a few pieces of added zinc, I noticed that when the acid became tolerably concentrated sulphur separated in small quantity. Repeating and modifying the experiment, I found that if zinc, either alone or along with hæmatite, be placed in boiling sulphuric acid, of the strength 2 vols. water to 1 vol. acid, a point is reached after a time at which the evolution of hydrogen visibly slackens, and sulphur begins to separate on the sides of the vessel. If more dilute acid be employed, boiling must be continued for a longer time than when stronger acid is used.

A marked modification in the process of change thus occurs at a certain degree of concentration of the reacting bodies and at a certain temperature.

I should be inclined to regard the production of sulphur as due to at least two reactions, viz., the direct reduction of molecules of H_2SO_4 to H_2O and S by nascent hydrogen, and the deoxidation of molecules of SO_3 , undoubtedly present in the hot concentrated acid, by zinc or zinc oxide.*

7. It is well known that certain chemical changes, which proceed with rapidity under conditions such that a secondary change is possible, proceed at a greatly diminished rate, or sometimes apparently cease altogether, when the secondary change is prevented from occurring.

Now we may regard such changes as really proceeding to a small extent even when the happening of the secondary change is rendered impossible. But the whole system is quickly brought into a strained condition, and the change stops; let, however, the secondary action now occur, the strain is relieved and the primary action proceeds.

As an example of such modifying influence of a secondary change I annex the results of experiments made on the solvent action of sulphuric acid on ferric oxide under different conditions.

It is known that the rate at which sulphuric acid dissolves ferric oxide is materially increased by adding a few pieces of zinc to the mixture of acid and oxide.

A series of experiments was made on the solvent action of sulphuric

* The experiment described has also, I think, a bearing on the question of the action of metals on acids: just as in the experiment described by Gladstone and Tribe on p. 179 of this Journal [1879, *Proc.*], the hydrogen, displaced from nitric acid by magnesium, was obtained along with one or more of the products of the reduction of the acid itself by hydrogen, so here we have the simultaneous production of hydrogen, and a product of the reduction of sulphuric acid by hydrogen, viz., sulphur.

acid of various strengths on very finely divided ferric oxide previously heated for 10 minutes over a Bunsen lamp: the acid was used alone, in conjunction with zinc, and aided by the passage through it of an electric current from two Grove's cells. The results, however, were nearly alike in each case; the ferric oxide dissolved in from 10 to 12 minutes.

The ferric oxide was again heated in small successive quantities for 20 minutes over a large Bunsen lamp, and then for 5 minutes over the blowpipe.

0.42 gram dissolved in boiling sulphuric acid (6 water to 1 acid by volume) in 35 minutes.

0.42 gram dissolved in boiling sulphuric acid (6 water to 1 acid by volume) with addition of 3 grams of pure zinc in 20 minutes.

A sample of brown hæmatite in fine powder was subjected to the action of acid of strength 3 : 1 :—

0.26 gram dissolved in 35 minutes, when no zinc was added.

0.26 " " 15 " when 3 grams zinc were added.

0.26 " " 25 " when the current from two Grove's cells was passed through the acid during the action.

Now as both ferric and ferrous sulphate are soluble salts, it would appear that the removal of the product of the primary action (even when soluble under the experimental conditions as in this case) causes that action to proceed at an accelerated rate.

The decomposition of each molecule of ferric sulphate as soon as produced by the nascent hydrogen would of course set free a molecule of sulphuric acid ready to react on a fresh portion of ferric oxide, and moreover this acid would come in contact with ferric oxide just as it was liberated from a compound, and in this condition compounds as well as elements appear capable of bringing about chemical changes which they cannot originate under ordinary conditions.

8. A consideration of chemical equilibrium from a dynamical point of view thus leads, I think, to the conclusion that chemical changes are always complex; that each change consists of at least two parts—a direct and a reverse change—that during the progress of either of these, secondary changes may be induced which will in their turn modify the primary changes; that systems not in phases of absolute stability tend to undergo change by contact with very minute quantities of matter in phases other than their own;* such systems

* See paper by Gibbs already referred to.

will always tend to pass into that phase in the passage to which the maximum loss of entropy (or gain of entropy if the term be used in the Clausian sense) occurs; but that this tendency may to a certain extent be prevented by the action of impressed force.

"Chemical induction" would in this view of chemical action be of much more frequent occurrence than is generally supposed; indeed it would be a part of every chemical change, becoming, however, more marked in some changes than in others.

By thus extending the meaning of the phrase "chemical induction" we should, I think, find certain analogies between electrical and chemical induction phenomena. Just as electrostatic induction is known to consist in a strained state of the medium, so chemical induction would also involve a state of strain in the reacting system; and as the breakdown of electrostatic induction produces the phenomenon of conduction, so would the breakdown of the strain in a chemically reacting system be accompanied by a process of chemical change. Further the strained medium would in each case be endowed with potential energy, which would become kinetic on the removal of the strain; and once more mechanical agitation might be regarded as probably favourable to the progress of a chemical change, just as it causes a more rapid recovery of a medium which has been strained by the process of electric induction.

XXIX.—*On the Influence of the Amido-group upon the Orientation of Bromine or NO₂ in the Benzene-nucleus, as illustrated by the preparation of the six possible Dibromotoluenes, the six possible Tribromotoluenes, the three possible Tetrabromotoluenes, and various other Bromo- and Bromonitro-derivatives of Toluene.*

By R. H. C. NEVILE and A. WINTHER.

In the table given in his memoir on the "Isomerism of the Aromatic Compounds containing Six Atoms of Carbon," Körner (*Gazzetta chim. ital.*, 1874, 305; *Chem. Soc. J.* [2], 14, 204; *Jahresb.*, 1875, 364) lays down the rule that when one of the halogens or the nitro-group is introduced into aniline, it takes the para-position. Körner's paper deals only with the substitution of the second hydrogen-atom in mono-derivatives of benzene, and consequently in this case only with aniline. But it appears to us for various reasons that the rule is of more general application, and that if bromine or another halogen, or the nitro-group,

be directly introduced into aniline or any of its homologues, such as toluidine or xylidine, and very probably other amido-compounds, the acid-group nearly always, if possible, takes the para-position to the amido-group; or if the para-position be occupied by any other group that it then takes one of the ortho-positions, but that under no circumstances can one of the above groups be directly introduced into a position meta to the amido-group.

We have investigated this question carefully only so far as relates to the monamido-compounds. We are inclined to think that the same rule will hold good with reference to diamido-compounds and others, but the data we have at the present time are not sufficient to enable us to arrive at a definite conclusion on this point.

The only experiments that we have noticed which appear to point to conclusions at variance with the above theory, are some experiments of E. Wroblewsky's (*Jahresb.*, 1870, 528; 1871, 450; summary in *Liebig's Annalen*, 168, 147) on the formation of the six possible isomeric dibromotoluenes. As some of these results point to a conclusion directly opposed to the above theory in both its branches, we have thought it wise to repeat the experiments, and have done so with results which seem to us to establish the correctness of the above conclusion as against the experiments of Wroblewsky.

We will consider first the two possible ortho-meta-dibromotoluenes, viz., 1 : 2 : 3 and 1 : 2 : 5.

Wroblewsky states that he has succeeded in preparing both of these, and in the following ways:—The first from the diazoperbromide of metabromorthotoluidine; the second from the diazoperbromide of orthobromometatoluidine, by heating them respectively with absolute alcohol.

He describes them as different substances, and says that the first is a liquid boiling at 238—239°, and giving on nitration a mononitro-compound melting at 86—87°, and convertible by reduction into an amido-compound melting at 83°; and he says further that a similar compound can be obtained by brominating metabromotoluene. As to the product of the second reaction, he says that it is solid (m. p. 42·5°, b. p. 239°). Further that he gets the same compound by removing the amido-group from dibromorthotoluidine, and that this latter gives a nitro-compound melting at 59°. He assigns to the former the constitution 1 : 2 : 3, and to the latter the constitution 1 : 2 : 5, without, as far as we have been able to ascertain, giving any reasons.

Now it is clear that the above results, if true, are opposed to the theory enunciated before as to the bromine taking the para-position to the amido-group, as if it did so the two dibromotoluenes would evidently be identical, as in fact we believe them to be.

We prepared the dibromotoluene both from orthobromometatoluidine

and from metabromorthotoluidine (we also obtained the dibromotoluene from dibromorthotoluidine, but found it quite different, and shall speak of it later). As to the former we proceeded as follows:—

By acting upon acetorthotoluid with a single molecular proportion of bromine suspended in water, we obtained a monobromacetotoluid, which, by decomposition with alcoholic potash, gave a monobromotoluidine, which, after separation from small quantities of dibromotoluidine, formed by solution in *dilute* hydrochloric acid and reprecipitation with sodic carbonate and purification by distillation with steam, melted at 55—56° (Wroblewsky gives 58°). This monobromotoluidine was converted into diazoperbromide, and decomposed by warming it gently with glacial acetic acid. We thus obtained the dibromotoluene.

We proceeded in the same way to obtain it from metatoluidine, also, however, boiling the hydrochloric acid solution of monobromometatoluidine to expel any dibromotoluidine that had been formed, as we found that, although it is far more soluble in dilute acids than the corresponding dibromorthotoluidine, it nevertheless distils away freely from the solution.

Here, however, we find a divergence from Wroblewsky's results. He states that the monobromometatoluidine obtained by the decomposition of the monobromacetometatoluid with alcoholic potash is an oil. We, however, found it to be a solid of m.p. 77—78°:—

Analysis:—

Employed .. 0.2005 AgBr = 0.2031 = 43.10 per cent. Br.

„ .. 0.2497 AgBr = 0.2536 = 43.21 „

The theory for $C_6H_5.CH_3.NH_2.Br$ requires 43.01 per cent. Br.

On converting this into diazoperbromide and decomposing it in the same way as the compound from orthotoluidine, we likewise obtained a dibromotoluene. We also prepared the monobromometatoluidine in the following way:—Taking metanitroorthotoluidine, we converted it into diazoperbromide, and decomposed it with warm acetic acid. In this way we obtained metanitroorthobromotoluene, which, after distillation with steam and frequent recrystallisation from alcohol, melted at 76.3°:—

Analysis:—

Employed .. 0.3217 AgBr = 0.2783 = 36.81 per cent. Br.

Theory for $C_6H_5.CH_3.Br.NO_2$ requires 37.04 per cent. Br.

On reducing this with tin and hydrochloric acid and distilling the product with steam, we obtained a monobromometatoluidine, melting at 76—78.5°.

We consider the dibromotoluenes prepared by either of the methods given above as identical, for the following reasons:—

1st. They are both fluid at ordinary temperatures, and do not solidify in a freezing mixture of ice and salt.

2nd. On nitrating them with fuming nitric acid, sp. gr. 1520 :—

That from metatoluidine gave a compound, m. p. 87·6—88·5°.

That from orthotoluidine gave a compound, m. p. 88·2—88·6°.

3rd. On reducing these nitro-compounds with iron and acetic acid, they gave amido-compounds :—

That from metatoluidine melted at 84—85°.

That from orthotoluidine „ 84·5—85·1°.

These experiments, as we consider, establish without doubt that the dibromotoluenes produced either from metabromortho-diazotoluene perbromide or orthobromo-meta diazotoluene perbromide are identical, and must consequently be ortho-meta-derivatives, viz., either 1 : 2 : 5 or 1 : 2 : 3, showing also that when bromine is introduced into orthotoluidine, it takes the meta-position relatively to CH_3 , and when introduced into metatoluidine, it takes the ortho-position.

As these two methods give only one dibromotoluene, we next endeavoured to prepare the other one of the orthometa-constitution. We proceeded thus :—Taking metanitrororthotoluidine (m. p. 128°), we suspended it in water, and added a solution of bromine in water to the amount of slightly more than a single molecular proportion, leaving the mixture to itself for some time, and finally warming it slightly. By then filtering off the liquid, washing, and drying the residue, we obtained a substance, which, after recrystallisation from alcohol, melted at 180·3—181·3° (corr.) :—

Analysis :—

Employed .. $0\cdot1957 \text{ AgBr} = 0\cdot1577 = 34\cdot29 \text{ per cent. Br.}$

Theory for $\text{C}_6\text{H}_2\cdot\text{CH}_3\cdot\text{NH}_2\cdot\text{Br}\cdot\text{NO}_2$ requires 34·63 per cent. Br.

This substance is therefore bromonitrororthotoluidine, and is different from that which Wroblewsky obtained, by nitrating metabromortho-acetatoluid, and taking out the acetyl group, for which he gives the melting point 139°.

We investigated the constitution of this substance as follows :—We prepared also the compound described by Wroblewsky as of m. p. 139°, and also the bromonitroparatoluidine in two ways, viz., by first nitrating and then brominating, and also by first brominating and then nitrating. (It is probably unnecessary to mention that one must use the acetyl-compound for nitration, but that the aceto-group must be taken out before bromine can be introduced into the nitro-compound.) We treated the above four compounds with nitrous gas and alcohol, to remove the amido-group, and then reduced the bromonitrotoluene thus produced with tin and hydrochloric acid. The bromotoluidine thus

produced was also converted into an aceto-compound by boiling with glacial acetic acid for seven or eight hours, with the results tabulated below :—

	From ortho- toluidine by first nitrating and then bromi- nating.	From ortho- toluidine by first brominating and then nitrating.	From para- toluidine by first nitrating and then brominat- ing.	From para- toluidine by first bromi- nating and then nitrating.
Nitrobromotolui- dine	m.p. 180·3—181·3°	m.p. 143·0°	m.p. 64—65°	m.p. unpurified, 63°
Nitrobromotoluene	81·4—81·8°	81·4—81·8°	81·4—81·8°	81—81·5°
Bromotoluidine ..	35·6—36°	34·5—37°	36·6°	35—35·2°
Aceto-compound of the bromotolui- dine	167—168°	167—168°	167—168°	168°

Hence it is clear, as we think, that the bromonitrotoluenes, as obtained by the four methods above mentioned, are identical. As to the bromotoluidine, the melting points differ slightly, and Wroblewsky says that this compound (as obtained from the bromnitroparatoluidine) is a liquid. Ours remained liquid for a long time, and at last solidified only after a very cold night. We then found, however, that the smallest particle of the crystalline substance was sufficient to make any quantity crystallise at once. We found it, however, pretty nearly impossible to recrystallise it from alcohol, as it declined to crystallise at all until nearly all the alcohol had evaporated, and then generally the whole became solid at once. This will account for the slight differences in the melting points. Now we have already shown that bromine assumes the meta-position to CH_3 in orthotoluidine, and it is known that the nitro-group also takes up the meta-position relatively to CH_3 in both ortho- and para-toluidine. Hence the bromonitrotoluene must have the constitution 1 : 3 : 5. This shows also that on the introduction of bromine into paratoluidine, it takes a position meta to CH_3 .

We see, then, that of the first two bromonitrotoluidines, one must have the constitution $\text{CH}_3\text{NH}_2\text{Br}\cdot\text{NO}_2$, and the other the constitution $\text{CH}_3\text{NH}_2\text{NO}_2\text{Br}$. We now proceeded to convert the meta-bromometanitroorthotoluidine, melting at 180·3—181·3°, into meta-bromometanitroorthobromotoluene by decomposing the diazoperbrom-

mide by warming it with glacial acetic acid. We thus obtained dibromonitrotoluene melting at 105.4° .

Analysis :—

Employed.. $0.2378 \text{ AgBr} = 0.3025 = 54.13 \text{ per cent. Br.}$

Theory for $\text{C}_6\text{H}_2\text{CH}_3\text{Br}_2\text{NO}_2$ requires $54.23 \text{ per cent. Br.}$

On reducing this with iron and acetic acid, and distilling the separated base with steam, we obtained a dibromotoluidine, melting at 86.4° . This compound dissolves in hot dilute hydrochloric acid with tolerable facility, and the salt crystallises out on cooling in small white needles.

Analysis for free HCl:—

Employed.. $0.0808 \text{ AgCl} = 0.0382 = 11.69 \text{ per cent. Cl.}$

Theory for $\text{C}_6\text{H}_2\text{CH}_3\text{Br}_2\text{NH}_2\text{HCl}$ requires $11.77 \text{ per cent. Cl.}$

On heating this dibromotoluidine with glacial acetic acid for six or seven hours, it is converted into an acetyl-compound, which, after purification with animal charcoal and recrystallisation from alcohol, melts at $204\text{--}205^{\circ}$.

On treating the dibromotoluidine with nitrous gas and alcohol to remove the amido-group, we obtained a substance which, after distillation with steam, melted at $27.4\text{--}27.8^{\circ}$; and on dissolving this in a mixture of three volumes of nitric acid of sp. gr. 1.520 and one volume of sp. gr. 1.450, and precipitating with water, we obtained a nitro-compound melting at $51\text{--}62^{\circ}$.

Following up our theory that bromine will take up a position para to the amido-group, we now endeavoured to prepare the above substance (which we shall show to be in all probability 1 : 2 : 3 dibromotoluene) from the aceto-metabromometatoluid described above as of m. p. $167\text{--}168^{\circ}$. We acted upon it with a single molecular proportion of bromine in aqueous solution. The bromine was at first absorbed with tolerable rapidity, but towards the end of the reaction it became necessary to apply heat in order to cause complete absorption. Thus we obtained a dibromacetoluid of m. p. $204\text{--}205^{\circ}$. On heating this with a mixture of equal volumes of hydric sulphate and water, it was decomposed, and on diluting with water and cooling, the sulphate of a dibromotoluidine crystallised out. On decomposing this with sodic carbonate, we obtained the dibromotoluidine, melting, after recrystallisation from alcohol, at $83\text{--}85^{\circ}$. On decomposing this with nitrous gas and alcohol, and distilling the product with steam, we obtained a substance, melting at $27.4\text{--}28^{\circ}$.

Analysis :—

Employed.. $0.2675 \text{ AgBr} = 0.4 = 63.63 \text{ per cent. Br.}$

Theory for dibromotoluene requires 64·00 per cent. Br.

On nitrating this with a mixture of three volumes 1520, and one volume 1450, nitric acid, we obtained a nitro-compound, which, after several recrystallisations from alcohol, melted at 56·5—57·5°.

Analysis:—

Employed.. $0\cdot2048 \text{ AgBr} = 0\cdot2613 = 54\cdot29$ per cent. Br.

Theory for $\text{C}_6\text{H}_2\cdot\text{CH}_3\cdot\text{Br}\cdot\text{Br}\cdot\text{NO}_2$ requires 54·24 per cent. Br.

This, reduced with tin and hydrochloric acid, gave an amido-compound, which, after crystallisation from alcohol, melted at 52—53°.

From the above it is clear that the two methods employed by us give identically the same results, and that this is the other ortho-meta-dibromotoluene.

There now only remains the question, which of the two dibromotoluenes we have described has the constitution $\text{CH} : \text{Br} : \text{Br} = 1 : 2 : 5$, and which $1 : 2 : 3$.

We endeavoured to decide this point by converting them into dibromobenzoic acids by heating them with dilute nitric acid (one vol. 1360 to three of water) for about three days. In this way we obtained from the one first described:—From the portion prepared from meta-toluidine a dibromobenzoic acid, melting at 149—151°. (On analysis this gave 57·49 per cent. Br; theory requiring for dibromobenzoic acid 57·14 per cent. Br.) From the portion prepared from ortho-toluidine, a dibromobenzoic acid, melting at 151—153°. (On analysis this gave 58·40 per cent. Br.) From the dibromotoluene last described, we obtained a dibromobenzoic acid, melting at 146—148°.

Analysis:—

Employed.. $0\cdot1372 \text{ AgBr} = 0\cdot1847 = 57\cdot35$ per cent. Br.

The first agrees very closely with that described by V. v. Richter (*Ber.*, 1875, 1422; *Jahresb.*, 1875, 293), as obtained from paradibromobenzene, and melting at 151—152°; and on distilling some of it with lime, we obtained a very small quantity (unfortunately not sufficient for analysis) of a solid, resembling in outward appearance paradibromobenzene, and melting at 85—86°, the melting point of paradibromobenzene when pure being 89°.

Although the above differences in the melting points of the benzoic acids taken by themselves would not, in our opinion, be sufficient to settle the question as to the constitution of the two dibromotoluenes from which they are obtained, yet, taken in connection with the fact that from the former, on distillation with lime, the above solid was obtained, we think we may safely conclude that the former has the two bromine-atoms in a position para to each other, and consequently has the constitution $1 : 2 : 5$, and the latter consequently the consti-

tution 1 : 2 : 3; more especially as if we assign to them the opposite constitutions, we must imagine that both in orthotoluidine and in metatoluidine both the bromine and also the nitro-group when introduced takes a position ortho to NH_2 rather than para, which would be exactly contrary to Körner's results in the case of aniline, and could not be the result of the influence of the CH_3 -group, inasmuch as the negative group is in either case meta thereto.

If, then, we accept the above theory of the constitution of the two compounds, it will be seen that throughout the above reactions the bromine and nitro-groups follow the laws indicated in the theory at the commencement of this paper, the bromonitrotoluidine obtained by us (m. p. 180—183°) having the constitution $\text{CH}_3.\text{NH}_2.\text{Br}.\text{NO}_2$, and that obtained by Wroblewsky (m. p. 139°) the constitution $\text{CH}_3.\text{NH}_2.\text{NO}_2.\text{Br}$, and ordinary nitrotholuidine the constitution $\text{CH}_3.\text{NH}_2.\text{NO}_2$.

We next consider what we may call symmetrical dibromotoluene, in which both the bromine-atoms are meta to the CH_3 -group.

This we obtained, contrary to the observation of Wroblewsky, both from dibromortho- and from dibromo-paratoluidine.

Our results were as follows :—

1st. With orthotoluidine. By acting upon this either in alcoholic or in acid aqueous solution with a slight excess of bromine, we obtained (after precipitation with water in the former case, and after distillation with steam) a white crystalline dibromotoluidine, which melted constantly at 45–46° (the melting point given by Wroblewsky is 50°).

Analysis :—

Employed.. $0.4472 \text{ AgBr} = 0.6328 = 60.19 \text{ per cent. Br.}$

Theory for $C_6H_2.CH_3.Br_2.NH_2$ requires 60.37 per cent. Br.

Wroblewsky states that this compound does not combine with acids. We found that it did not unite with dilute acids; but by heating it with strong acids we formed the sulphate, nitrate, and chloride, and found that at all events the latter could be recrystallised from alcohol or suspended in cold water, without apparent decomposition. Heating with water at once caused the resolution of the salt into the base and free acid.

Acting in a similar manner with bromine on paratoluidine we obtained a dibromotoluidine melting at 73° (Wroblewsky gives 76°).

Analysis :—

Employed.. $0.3237 \text{ AgBr} = 0.4549 = 59.79 \text{ per cent. Br.}$

On acting upon the above dibromotoluidines with a solution of nitrous

acid in alcohol, the first gave, after distillation with steam, at once a substance melting at 39°.

Analysis:—

Employed .. 0·4761 AgBr = 0·7194 = 64·29 per cent. Br.

Theory for $C_6H_3.CH_3.Br_2$ requires 64·00 per cent. Br.

The second, obtained from paratoluidine, gave a substance which generally melted a little higher, viz., at 40—42°, but could be easily separated by recrystallisation into two substances, one of which melted at 39°, and was in all appearances exactly similar to the one above described.

Analysis:—

Employed .. 0·4728 AgBr = 0·7121 = 64·09 per cent. Br.

The other (present only in very small quantities) melted at or above 121°. This latter was probably a bye-product of the action of the nitrous gas, probably an amidoazo-compound, but the quantity obtained was not sufficient to enable us to make any examination of it.

On treating the dibromotoluenes with fuming nitric acid, and precipitating the products with water, they both gave nitro-compounds, melting at first from 120—125°; by several recrystallisations from alcohol these were separated into two compounds:—

	(α) From orthotoluidine.	(β) From paratoluidine.
1. Melting point	157·8—158·3°	157·6—158°
2. ,, 	105°	105°

These both proved on analysis to be dinitro-compounds.

Analysis:—

1. α. Employed.. 0·2192 AgBr = 0·2417 = 46·92 per cent. Br.

Theory for dibromodinitrotoluene requires 47·05 per cent. Br.

1. β. Employed.. 0·2356; N = 16·5 c.c.; *b* = 758·4; *t* = 17·1
= 8·1 per cent. N.

2. β. Employed.. 0·1351; N = 9·25 c.c.; *b* = 755·7; *t* = 17·0
= 7·89 per cent. N.

Theory for dibromodinitrotoluene requires 8·23 per cent. N.

Further, in both cases the dibromotoluene, melting at 39°, gave on oxidation with chromic and acetic acids a benzoic acid melting between 207° and 210°.

Analyses—

From ortho. Employed.. 0·1551 AgBr = 0·2117 = 58·08 per cent. Br.

From para. Employed .. 0·1603 AgBr = 0·2187 = 58·05 per cent. Br.

All the above results seem to show conclusively that in the action of bromine upon either ortho- or para-toluidine, the bromine-atoms

take up the same positions, one of which we already know to be meta to CH_3 . As to the position of the second, it must either be the other meta-position or the ortho-position, and the dibromotoluene must have either the constitution 1 : 2 : 3; 1 : 2 : 5; or 1 : 3 : 5. We have already described the first two, and their characteristics are quite different, and therefore the only constitution remaining is 1 : 3 : 5.

Further, the dibromobenzoic acid agrees with that described by V. v. Richter (*Ber.*, 1875, 1423), as obtained from metadibromobenzene of melting point 208—209°.

It may be well here to notice a statement made by Gerver (*Jahresb.*, 1873, 674), who says in a footnote, that he obtains from orthotoluidine, by the action of 3 molecules of bromine, a tribromotoluidine which melts at 105—106°, and from a weak alcoholic solution with 1 molecule of bromine, a mixture of di- and tri-bromotoluidines melting at 85—89°.

Owing to this statement we have made most careful experiments, both in alcoholic and ethereal solutions, as well as in aqueous acid solutions, but we could never obtain from ortho- or para-toluidine any more highly brominated toluidine than a dibromotoluidine. Any further bromine either remained uncombined or acted upon the solvents, generally producing a pitch which entirely declined to distil with steam or to give any crystals on extraction with dilute alcohol. In fact, when sufficient bromine was added, the whole of the dibromotoluidine was destroyed if in aqueous solution.

We also tried the same substance without any solvents with similar results, the excess of bromine remaining uncombined.

We can only account for Gerver's statement by supposing that the orthotoluidine he used was impure, and with reference to this point we would observe that the melting point of the aceto-compound of orthotoluidine seems to be by no means a sufficient proof of its purity, inasmuch as Hübner and Wallach (*Jahresb.*, 1869, 678) find 105—106° for the melting point of an acetotoluid, which Rosenstiehl considers to be a mixture of orthotoluid with about 30 per cent. of paratoluid, and which, from the method of preparation given by H. and W., we should imagine to be anything but a pure orthotoluidine. It is, therefore, by no means impossible that the compound used by Gerver may have contained metatoluidine or aniline, which do give with bromine tribromo-compounds.

We now come to the parabromometabromotoluene (1 : 3 : 4).

This we prepared from monobromoparatoluidine by means of the diazoperbromide reaction. We found this monobromotoluidine to be, as described by Wroblewsky, an oil, and we can also confirm his results as to the dibromotoluene. It was fluid.

Analysis:—

Employed .. 0.2666 AgBr = 0.4031 = 64.34 per cent. Br.

On nitrating it with fuming nitric acid, we got a crystalline compound (as well as a very small quantity of an oil) melting, after frequent recrystallisations from alcohol, at 86.6—87.5°.

Analysis:—

Employed .. 0.1240 AgBr = 0.1586 = 54.42 per cent. Br.

On reducing this with iron and acetic acid we obtained a compound which, after distillation with steam, dissolution in dilute hydrochloric acid, and reprecipitation with sodic carbonate, melted at 96.8—98°.

Analysis:—

Employed .. 0.2942 AgBr = 0.4185 = 60.53 per cent. Br.

We also converted this dibromotoluene into a dibromobenzoic acid by oxidation with chromic and acetic acids; this, after purification by conversion into barium salt, washing with ether, and reprecipitation with hydrochloric acid, melted at 232—233°.

Analysis of the barium salt:—

Employed .. 0.3119 AgBr = 0.3300 = 45.02 per cent. Br.

Theory for dibromobenzoate of barium 46.04 per cent. Br.

The melting point given by Burghardt (*Ber.*, 1875, 558) is 229—230°.

We now come to the last two, viz., 1 : 2 : 4 and 1 : 2 : 6. Here again our results differ from those of Wroblewsky. He prepares the latter from the dibromometatoluidine resulting from the action of two molecular proportions of bromine on acetometatoluidine and subsequent decomposition with alcoholic potash. He describes the dibromotoluidine as of melting point 92.5°; and the dibromotoluene resulting from it by elimination of the amido-group as liquid and boiling at 246°. By nitration of the dibromotoluene he obtains a mononitro-compound melting at 79°.

We find that on acting upon the aceto-compound of metatoluidine with two molecular proportions of bromine, the first one is readily absorbed, forming a monobromaceto-compound, but the last one is absorbed with much greater difficulty, giving at last a dibromaceto-compound which, however, on the removal of the acetyl-group with alcoholic potash was proved to give, not one, but a mixture of two dibromotoluidines; a small quantity of tri-bromotoluidine was also always formed at the same time.

We separated these as follows:—The di- and tri-bromotoluidines were distilled off from dilute acid which retained the monobromotoluidine.

This, after separation from the acid solution by means of sodic carbonate, melted at 76—77°.

The mixed di- and tri-bromotoluidines were then extracted with hot strong hydrochloric acid. The liquid on cooling deposited crystals.

Analysis :—

Employed .. 0.1993 AgBr = 0.3117 = 66.54 per cent. Br.

Theory for dibromotoluidine 60.38 per cent.

„ tribromotoluidine 69.76 „

Whence it appears that the crystals consist of a mixture of di- and tri-bromotoluidine; on distilling them with steam, a distillate of lower melting point (78—84°) came over first, followed by a portion of higher melting point (98—99°). We found the melting point of the tribromometatoluidine, prepared by the direct action of bromine upon an acid solution of metatoluidine, after purification, to be 100—101.6°. (Wroblewsky gives 97°.) The portion which had remained undissolved in hydrochloric acid was repeatedly distilled with steam, rejecting the last portions. The distillate thus purified was recrystallised from alcohol, and thus we obtained one portion (the largest by far) of m. p. 74.6—75.5°. This appeared to consist of a single dibromotoluidine.

Analysis :—

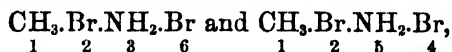
Employed .. 0.2241 AgBr = 0.3207 = 60.89 per cent. Br.

Theory requires 60.38 per cent. Br.

On boiling it with glacial acetic acid for 30 or 40 hours, it gave an acetyl-compound which, after purification and recrystallisation, melted at 168—168.6°.

The mother-liquids contained a substance of lower melting point, 33—35°.

According to the theory laid down at the beginning of this paper, two different dibromotoluidines could be produced, viz.,



and we concluded that in all probability these were the two, although we could not be sure of their purity.

We now converted them into dibromotoluenes, and from the first (m. p. 74.6—75.5°) we obtained an oil which did not solidify at -20°.

Analysis :—

Employed .. 0.1871 AgBr = 0.2834 = 64.32 per cent. Br.

On nitration at ordinary temperatures without cooling, this gave a mixture of nitro-compounds separable by recrystallisation from alcohol into one of melting point 80—80.6°, crystallising in white needles.

Analysis :—

Employed .. 0.2512 AgBr = 0.3248 = 55.01 per cent. Br.

Analysis of a portion melting lower, 75—80° :—

Employed .. 0.1396 AgBr = 0.1741 = 53.06 per cent. Br.

Theory for mononitrodibromotoluene being 54.23 per cent. Br, and another of higher melting point, 128—129°, which proved on analysis to be a mixture of di- and tri-nitrodibromotoluene : this crystallised in scales.

Analysis :—

Employed .. 0.1685 AgBr = 0.1765 = 44.57 per cent. Br.

„ .. 0.0762 AgBr = 0.0787 = 43.94 „

Theory for dinitrodibromotoluol requires 47.05 per cent. Br ; theory for trinitrodibromotoluol requires 41.04 per cent. Br. Also a substance in small quantity melting below 80°.

We also converted this dibromotoluene into a dibromobenzoic acid by heating it with dilute hydric nitrate, and thus obtained one which after purification melted at 167—169°.

Analysis :—

Employed .. 0.0722 AgBr = 0.0959 = 56.52 per cent. Br.

Theory for dibromobenzoic acid requires 57.14 per cent. Br.

If the dibromotoluene was kept cool by cold water during nitration the trinitro-compound did not appear to be formed.

From the other substance (m. p. 33—35°) we also obtained by removal of the amido-group, an oil which did not solidify at -20°. This gave on nitration a mixture which by recrystallisation from alcohol we separated into a compound melting at 159—161°, and not freely soluble in alcohol, from which it crystallised in long fine needles ; and another in small quantity melting below 80°. This dibromotoluene when heated with nitric acid also gave a dibromobenzoic acid melting at 150—167°.

The behaviour of these two dibromotoluenes with fuming nitric acid shows that they are different from any of the four above described, and therefore that their constitutions must be 1 : 2 : 4 and 1 : 2 : 6. The question remains as to which is which. To determine this we endeavoured to prepare them in other ways. For the preparation of 1 : 2 : 4 we took ordinary dinitrotoluene (m. p. 70°) which is known to have this constitution ; from it we prepared orthonitroparatoluidine (m. p. 77—78°) by reduction with alcoholic ammonium sulphide ; from this we obtained orthonitroparabromotoluene (m. p. 44.4—45.2°) by the diazoperbromide reaction. This crystallised in beautiful large monoclinic tables, which on reduction gave parabromorthotoluidine

(m. p. 30—31°); and this by the diazoperbromide reaction gave us 1 : 2 : 4 dibromotoluene. This, after removal of some adhering cresol by potassic hydrate and distillation with steam, proved to be an oil not solidifying at -20°. On nitrating it with fuming nitric acid, and recrystallising the product from alcohol, needles were obtained melting at 80·5—81·3°.

Analysis:—

Employed .. 0·1596 AgBr = 0·2059 = 54·32 per cent. Br.

Another lot. The portion melting at 74—80° gave—

Employed .. 0·1472 AgBr = 0·1873 = 54·14 per cent. Br.

Some crystals in scales were also obtained, m. p. 128—129°.

Analysis:—

Employed .. 0·1314 AgBr = 0·1545 = 50·03 per cent. Br.

The dibromotoluene was also converted into dibromobenzoic acid by heating it with nitric acid. It crystallised from the acid solution in colourless tables in the same manner as the dibromobenzoic acid obtained from the first of the two above-described dibromotoluenes, and melted after purification at 168—170°.

Analysis:—

Employed .. 0·2461 AgBr = 0·3319 = 57·38 per cent. Br.

Theory requires 57·14 per cent.

This result agrees then very well with that obtained from the larger portion of the dibromometatoluidine, and points to the conclusion that the second atom of bromine takes up principally the position para to CH₃, a certain amount taking the ortho-position, and forming 1 : 2 : 3 : 6 dibromotoluidine.

To test the theory further, we endeavoured to prepare the 1 : 2 : 4 dibromotoluene in another way, viz., from 1 : 3 : 4 monobromotoluidine. This we prepared by the diazoperbromide reaction from mononitroparatoluidine. The metanitroparabromotoluene melted at 31—32°. This reduced with tin and hydrochloric acid gave an amido-compound which, after distillation with steam and recrystallisation from alcohol, melted at 30·6—32°.

Analysis:—

Employed .. 0·2063 AgBr = 0·2067 = 42·63 per cent. Br.

Theory for monobromotoluidine = 43·01.

Wroblewsky (*Jahresh.*, 1870, 527) says that it melts at 67°, but he also finds the bromnitrotoluene from which it is derived to be a liquid, and not solid at -20°. Hübner and Roos (*Ber.*, 1873, 800) say that it melts at 75°, although, they find the same melting point for the nitro-

bromotoluene as we do. We, however, prepared it several times, and always got very nearly the same melting point, and we cannot help thinking it possible that the parabromotoluene from which Hübner and Roos prepared their nitro-compound may have been mixed with some other bromotoluene, which may possibly have given metanitro-orthobromotoluene, and although this may not much have affected the melting point of the metanitroparabromotoluene, yet on reduction the amido-compound may have had a greater effect.

We next converted the bromotoluidine into aceto-compound by 30 or 40 hours' heating with the strongest glacial acetic acid with a reversed condenser. The product washed with water, freed from toluidine by extraction with hydrochloric acid, and recrystallised from water, melted at $113.7-114.6^{\circ}$. This was suspended in water, and two atomic proportions of bromine in aqueous solution added; the mixture was heated on a water-bath, but this was not found sufficient to cause complete absorption, and it was found necessary to redissolve the aceto-compound in alcohol and reprecipitate it with water, in order to get it into a sufficiently fine state of division; it then absorbed the bromine better. It was then decomposed by heating it with 2 vols. of sulphuric acid and one of water, precipitated with water, filtered, and the salt decomposed with sodic carbonate and distilled with steam. We thus obtained a dibromotoluidine which, after recrystallisation from alcohol, melted at $74.5-75.8^{\circ}$, and by boiling with glacial acetic acid for 30 to 40 hours, and subsequent purification, we obtained from it an aceto-compound melting at $168-168.6^{\circ}$.

The dibromotoluidine was now treated with nitrous gas and alcohol for the removal of the amido-group; an oil was thus obtained, which when heated with nitric acid gave a dibromobenzoic acid, m. p. $166-168^{\circ}$.

Analysis :—

Employed . . $0.2667 \text{ AgBr} = 0.3608 = 57.56 \text{ per cent. Br.}$

Theory requires 57.14 per cent.

On nitrating the dibromotoluene, needles were obtained melting at $78-80^{\circ}$.

These experiments then seem to confirm clearly the purity and constitution of the substance m. p. $74.5-75.5^{\circ}$ obtained from metatoluidine.

Fittig describes a dibromotoluene melting at $107-108^{\circ}$, which Wroblewsky considers to be $1:2:4$. We have been unable to obtain any dibromotoluene melting at this point or anywhere near it.

We now endeavoured to prepare the dibromotoluene $1:2:6$. We first tried to obtain it from dinitroparatoluidine, hoping to obtain therefrom a dinitrotoluene of the constitution $1:3:5$, and then by a

reduction, first of one and then of the other nitro-group, and intermediate bromination, to get first nitrometatoluidine ($\text{CH}_3.\text{NO}_2.\text{NH}_2$) then $\text{CH}_3.\text{Br}.\text{NO}_2.\text{NH}_2$ by introduction of bromine; then $\text{CH}_3.\text{Br}.\text{NO}_2$; then $\text{CH}_3.\text{Br}.\text{NH}_2$; next $\text{CH}_3.\text{Br}.\text{NH}_2.\text{Br}$; and finally $\text{CH}_3.\text{Br}.\text{Br}$.

In this, however, we were not successful, as up to the present we have not been able to get beyond the first step, as we have failed in taking out the amido-group from the dinitroparatoluidine. We have heated it with alcohol saturated with nitrous gas under a pressure of two atmospheres, and although a small quantity of substance has been obtained melting at $68-75^\circ$, yet the quantity is far too small to hold out any prospect of obtaining in this manner the desired dibromotoluene, except at an expenditure of time and material quite incommensurate with the object to be attained.

The second plan we tried promised better results. We took the acetyl compound of orthobromometatoluidine. This we nitrated by solution in a mixture of 1 volume nitric acid 1520 and 2 volumes 1450. It was then precipitated with water, washed, recrystallised from alcohol, m. p. $110-121^\circ$, and dissolved in a mixture of 2 vols. sulphuric acid and one of water by the aid of heat. This when cold was precipitated by water containing 1 molecular proportion of bromine in solution; in this way we obtained a dibromonitrometatoluidine which after crystallisation from alcohol melted at $124-130^\circ$.

Analysis:—

Employed .. 0.1220 AgBr = 0.1465 = 51.09 per cent. Br.
 „ .. 0.1975 AgBr = 0.2381 = 51.29 „

Theory, $\text{C}_6\text{H}_4.\text{CH}_3.\text{Br}_2.\text{NO}_2.\text{NH}_2$ = 51.61 per cent. Br.

In order to determine the constitution of the bromonitro-compound first obtained before the bromination (m. p. $110-121^\circ$) we dissolved it in a mixture of 2 volumes hydric sulphate and 1 volume water, precipitated with water, and recrystallised it from alcohol, thereby obtaining a compound of m. p. $179-181^\circ$.

Analysis:—

Employed .. 0.2060 AgBr = 0.1668 = 34.45 per cent. Br,
 together with a much smaller quantity of a substance of m. p. $102-103^\circ$.

Analysis:—

Employed .. 0.1587 AgBr = 0.1257 = 33.70 per cent. Br.

Theory for bromonitrotoluidine requires 34.63 per cent.

The portion melting at $179-181^\circ$ was treated with nitric acid and a current of nitrous acid, and gave on precipitation with a

solution of bromine in potassic bromine a yellow perbromide getting scarlet on drying. This decomposed with acetic acid and precipitated by water, and recrystallised from alcohol, melted at 87° .

Analysis :—

Employed .. 0.1076 AgBr = 0.1360 = 53.78 per cent. Br.

Theory for dibromonitrotoluene = 54.23 per cent.

This was reduced with iron and acetic acid, and gave on distillation an amido-compound which after crystallisation from alcohol melted at $84.6-85^{\circ}$.

Analysis :—

Employed .. 0.0895 AgBr = 0.1257 = 59.76 per cent. Br.

Theory for dibromotoluidine = 60.37 per cent. Br.

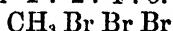
Some of this was converted into perbromide and decomposed with acetic acid, and thus gave crystals which after recrystallisation from alcohol melted at $110-111.5^{\circ}$.

Analysis :—

Employed .. 0.1158 AgBr = 0.1974 = 72.53 per cent. Br.

Theory for tribromotoluene = 72.94 per cent.

This agrees with a tribromotoluene which we shall show later to have the constitution 1 . 2 . 4 . 5.

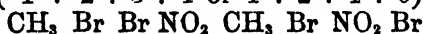


This shows that inasmuch as the positions 2 and 5 were occupied originally by bromine and the amido-group respectively, the nitro-group must have taken the position 4. Hence the constitution of the dibromonitrotoluene m. p. 87° must be $\text{CH}_3.\text{Br}.\text{NO}_2.\text{Br}$, and of the amido-compound m. p. $84.6-85^{\circ}$ $\text{CH}_3.\text{Br}.\text{NH}_2.\text{Br}$.

These compounds agree very closely with the dibromonitrotoluene and dibromotoluidine obtained from the dibromotoluene 1 . 2 . 5, and thus seem to show us that on nitrating that compound the NO_2 takes the position para to CH_3 .

This, then, shows us that the compound which we obtain by nitrating monobromometatoluidine must have the constitution $\text{CH}_3.\text{Br}.\text{NO}_2.\text{NH}_2$. On brominating this the two positions 3 and 6 are open, and therefore the compound produced must either be $\text{CH}_3.\text{Br}.\text{Br}.\text{NO}_2.\text{NH}_2$ or $\text{CH}_3.\text{Br}.\text{NO}_2.\text{NH}_2.\text{Br}$.

We now took out the amido-group by treating the dibromonitrotoluidine (m. p. $124-130^{\circ}$) with ethyl nitrite, and thus obtained a dibromonitrotoluene (1 . 2 . 3 . 4 or 1 . 2 . 4 . 6), melting at $56.8-57^{\circ}$.



Analysis:—

Employed .. 0·1489 AgBr = 0·1886 = 54·89 per cent. Br.

Theory requires 54·23 per cent. Br.

This, reduced with tin and hydrochloric acid, gave a dibromamido-compound melting at 87—88°.

Analysis:—

Employed .. 0·1376 AgBr = 0·1931 = 59·71 per cent. Br.

Theory for dibromotoluidine = 60·37 per cent.

On treating this with ethyl nitrite a dibromotoluene was obtained as an oil (not solidifying at -10°).

On dissolving it in nitric acid 1520 it became slightly warm and slowly dissolved. After some time strong colourless needles crystallised out. These, crystallised from alcohol, after purification with animal charcoal, melted at 161·6—162·2.

Analysis:—

Employed .. 0·1185 AgBr = 0·1303 = 46·78 per cent. Br.

„ .. 0·1690 AgBr = 0·1880 = 47·33 „

Mean = 47·05 per cent.

Theory for $C_6H_4.CH_3.Br_2(NO_2)_2$ is 47·06 per cent.

Now the above described dibromotoluene must, as we have shown, have either the constitution 1 : 2 : 3 or 1 : 2 : 6, and, as will be easily seen, it is quite different in its characteristics from the dibromotoluene 1 : 2 : 3 above described; it must therefore have the constitution 1 : 2 : 6. Moreover it agrees very closely with the dibromotoluene obtained from the dibromotoluidine of lower melting point, obtained from dibromometatoluidine, which we showed above must in all probability have this constitution.

TRIBROMOTOLUENES.

We have also prepared the six isomeric tribromotoluenes as follows:—

$C_6CH_3.Br.Br.H.Br.H$, from the diazoperbromide of dibromortho-toluidine. It crystallises from alcohol in long flat colourless needles, m. p. 52—53°.

Analysis:—

Employed .. 0·0993 AgBr = 0·1703 = 72·97 per cent. Br.

Theory for tribromotoluene requires 72·94 per cent.

Dissolved in nitric acid sp. gr. 1520 and precipitated with water, it gives a nitro-compound, which after crystallisation from alcohol melts at 95—170°.

$C_6H_5.H.Br.Br.Br.H$, from the diazoperbromide of dibromopara-dine, m. p. 88—89°.

Analysis :—

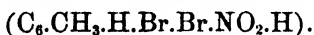
Employed .. 0.5161 $AgBr = 0.8866 = 73.07$ per cent. Br.

$C_6H_5.H.Br.Br.Br.H.Br$, from the diazoperbromide of the dibromo-metatoluidine m. p. 74—75.5°, which we showed before to have the constitution $C_6H_5.H.NH_2.Br.Br.H.Br$. It crystallises from alcohol in colourless long shining needles, m. p. 111.2—112.8°.

Analysis :—

Employed .. 0.4052 $AgBr = 0.6920 = 72.66$ per cent. Br.

$C_6H_5.Br.Br.Br.Br.H.H$. This was obtained as follows :—Metabromo-metanitroparatoluidine was converted into diazoperbromide, and from this metabrommetanitroparabromotoluene prepared—



This melted at 62—63.6°, and crystallised from alcohol in colourless leaves.

Analysis :—

Employed .. 0.3565 $AgBr = 0.4564 = 54.47$ per cent. Br.

Theory for dibromonitrotoluene = 54.24 per cent. Br.

This was reduced with iron and acetic acid, and gave an amido-compound which crystallised from alcohol in long colourless needles or flat prisms, m. p. 58—59°.

Analysis :—

Employed .. 0.3551 $AgBr = 0.5014 = 60.08$ per cent. Br.

Theory for dibromotoluidine = 60.37 per cent.

This was converted into aceto-compound of m. p. 162—163° by 24 hours' boiling with the strongest glacial acetic acid. It was then suspended in water and brominated. We thus obtained a tribromaceto-toluid, m. p. 171—173°, crystallising from alcohol in white needles. This decomposed with alcoholic potash gave a tribromotoluidine, m. p. 96—96.8°.

Analysis :—

Employed .. 0.0914 $AgBr = 0.1485 = 69.13$ per cent. Br.

Theory for tribromotoluidine = 69.76 per cent. Br.

This decomposed with nitrous acid and alcohol gave us a tribromo-toluene m. p. 44.4—44.7°.

Analysis :—

Employed .. 0.0965 $AgBr = 0.1636 = 72.14$ per cent. Br.

Theory for tribromotoluene = 72.94 per cent. Br.

On nitrating this by solution in nitric acid, sp. gr. 1.520, and pre-

precipitating with water, a nitro-compound is obtained, melting at first at 97—98°, but by frequent recrystallisations giving about 106—107° as m. p.

This sufficiently distinguishes this tribromotoluene from the one above described of m. p. 52—53°, and which gives a nitro-compound m. p. 95—170°.

$C_6H_3Br_3.H.H.Br.$ —This we obtained from Wroblewsky's bromonitrothotoluidine, m. p. 143°, which we showed above had the constitution $C_6H_3NH_2.NO_2.H.Br.H$, by converting it into dibromonitrotoluene by the diazoperbromide reaction. This melted at 69·5—70·2°.

Analysis:—

Employed.. 0·3090 $AgBr = 0·3959 = 54·51$ per cent. Br.

Theory 54·24 per cent. Br.

This we reduced with tin and hydrochloric acid, and thus obtained an amido-compound easily soluble in alcohol, m. p. 72·5—73·1°.

Analysis:—

Employed.. 0·1208 $AgBr = 0·1711 = 60·26$ per cent. Br.

Theory for dibromotoluidine = 60·37 per cent. Br.

This, boiled with glacial acetic acid, gave us an acetyl-compound, m. p. 144—145°. By suspending this in a state of fine division in water, and adding 2 atomic proportions of bromine, we obtained a tribromaceto-compound melting at 179—181°. On taking out the aceto-group from this by eight hours' boiling with alcoholic potash, we obtained a tribromotoluidine melting at 93—94°.

Analysis:—

Employed.. 0·1328 $AgBr = 0·2159 = 69·18$ per cent. Br.

Theory for tribromotoluidine requires 69·76 per cent. Br.

On treating this with nitrous gas and alcohol we obtained the tribromotoluene in flat needles melting at 58—59°.

Analysis:—

Employed.. 0·1238 $AgBr = 0·2128 = 73·13$ per cent. Br.

Theory for tribromotoluene = 72·94 per cent. Br.

Now, from the method of formation of this tribromotoluene it will be seen that it must have the constitution $C_6H_3Br_3.H.Br.Br.H$, or $C_6H_3Br_3.H.H.Br.Br.$ The former of these is the one obtained from dibromometatoluidine perbromide, and described above, m. p. 111·2—112·8°; therefore this one must have the latter constitution.

This tribromotoluene gives on nitration with nitric acid sp. gr. 1·520 a nitro-compound of m. p. 89—91°; recrystallised, 91—91·4°.

$C_6H_3Br_3.H.Br.H.Br.$ —This was prepared from tribromometatoluidine, melting at 100—101·6°.

Analysis:—

Employed.. 0.1629 $\text{AgBr} = 0.2650 = 69.22$ per cent. Br.

Theory for tribromotoluidine = 69.76 per cent. Br.

As this tribromotoluidine can be obtained by the bromination of the dibromometatoluidine, which we showed must have the constitution $\text{C}_6\text{H}_3\text{Br}_2\text{NH}_2$, it must have either the constitution $\text{C}_6\text{H}_3\text{Br}_3\text{NH}_2$, or $\text{C}_6\text{H}_3\text{Br}_2\text{NHBr}$; on decomposing it with alcohol and nitrous gas it gives a tribromotoluene which melts at 66° .

Analysis:—

Employed.. 0.1442 $\text{AgBr} = 0.2476 = 73.06$ per cent. Br.

Theory for tribromotoluene = 72.94 per cent. Br. This shows that it cannot have the constitution $\text{C}_6\text{H}_3\text{Br}_3\text{NH}_2$, for the tribromotoluene which would be derived from this is described above as melting at $44.4\text{--}44.7^\circ$.

On nitrating this tribromotoluene it gives a dinitro-compound melting at $217\text{--}220^\circ$.

Analysis:—

Employed.. 0.1106 $\text{AgBr} = 0.1499 = 57.66$ per cent. Br.

Theory for dinitrotribromotoluene = 57.28 per cent. Br.

TETRABROMOTOLUENES.

We have also prepared the three possible tetrabromotoluenes.

$\text{C}_6\text{H}_2\text{Br}_4$.—This we prepared from tetrabromometatoluidine, which we obtained by acting with bromine in aqueous solution upon a hydrochloric acid solution of metabromometatoluidine (m. p. $35\text{--}37^\circ$), we thus obtained a copious white flocculent precipitate which, after purification by boiling with animal charcoal in alcohol, in which it is not very soluble, crystallised therefrom in white needles, melting at $223\text{--}224^\circ$. This decomposed by boiling with alcohol and nitrous gas gave us a tetrabromotoluene melting at $105\text{--}108^\circ$.

Analysis:—

Employed.. 0.0763 $\text{AgBr} = 0.1403 = 78.24$ per cent. Br.

Theory requires for tetrabromotoluene 78.43 per cent. Br. This was also prepared from tribromometatoluidine perbromide, and was thus obtained of melting point $106.8\text{--}108^\circ$.

Analysis:—

Employed.. 0.2191 $\text{AgBr} = 0.4015 = 77.97$ per cent. Br.

On nitration with nitric acid, sp. gr. 1.520, precipitation with water and recrystallisation from alcohol, a nitro-compound was obtained melting at $215\text{--}216^\circ$.

$\text{C}_6\text{H}_2\text{Br}_4$.—This was obtained from tribromometatolu-

idine ($C_6H_3Br_3NH_2$, m. p. 93—94°, described on page 448) by the diazoperbromide reaction. In this way it was obtained of m. p. 116—117°.

Analysis:—

Employed .. 0.1041 $AgBr = 0.1924 = 78.64$ per cent. Br.

This nitrated with nitric acid, sp. gr. 1520, precipitated with water and recrystallised from alcohol, gave a nitro-compound melting at 213°.

$C_6H_3Br_3H$.—This was obtained from tribromometatoluidine ($C_6H_3Br_3NH_2$, m. p. 96—96.8°, described on page 447) by the diazo-perbromide reaction, and melted at 111.0—111.5°.

Analysis:—

Employed .. 0.1230 $AgBr = 0.2255 = 78.01$ per cent. Br.

This gave a nitro-compound melting at 212°.

Pentabromotoluene was obtained from the diazo-perbromide of tetrabromometatoluidine (m. p. 223—224°). After crystallisation from either acetic acid or alcohol, in neither of which is it freely soluble, and from both of which it crystallises in white needles, it melts at 283—285°.

Analysis:—

Employed .. 0.0918 $AgBr = 0.1782 = 82.59$ per cent. Br.

Theory requires 82.14 per cent. Br.

This agrees with the melting point (282—283°) given by Gustavson (*Bull. Soc. Chim.* [2], 28, 347).

In volume viii of Watts' Chemical Dictionary, p. 221, after some remarks on the melting points of the different nitro-, bromo-, and other derivatives of benzene, it is said "that the more symmetrical the constitution of a benzene-derivative, the greater is the resistance which it offers to the passage from the liquid to the solid state." This remark seems not to apply to the derivatives of toluene,* as the tribromotoluene ($C_6H_3Br_3H$) which, according to this, should melt the highest of the six tribromotoluenes, melts at 66°, while ($C_6H_3Br_3H$) and ($C_6H_3Br_3H$) both melt considerably higher.

We subjoin to this a table of the various bromine-derivatives of toluene, and hope to give in a future communication a further table of the other derivatives above described, together with some derivatives which we have not described.

In conclusion, we should like to make a few remarks upon some of the processes which we have used.

* The remark in question was intended to apply only to benzene-derivatives containing 6 atoms of carbon, the melting points of which are given in the volume above referred to (pp. 217—220).—H. W.

TABLE.

1	2	3	4	5	6		Product of nitration with HNO ₃ . Sp. gr. 1.520.	Product by reduction of above.	Benzoic Acid.
CH ₃	Br	—	—	—	—	Fluid, b. p. 182—183°..	{ These monobromotoluenes have not been investigated by us, as they appear to have been sufficiently previously investigated.	84—85° 52—53 — 97—98 — — — — — — — — — — — — — — — —	With HNO ₃ , 151—153° With HNO ₃ , 147—149° With CrO ₃ , 208—210° With CrO ₃ , 232—233° With HNO ₃ , 168—170° — — — — — — — — — — — — — — — —
CH ₃	—	Br	—	—	—	Fluid, b. p. 184°			
CH ₃	—	—	Br	—	—	M. p. 28° 5', b. p. 185° ..			
CH ₃	Br	—	—	Br	—	Fluid			
CH ₃	Br	—	—	—	—	M. p. 27° 4'—27° 8'			
CH ₃	—	Br	—	Br	—	M. p. 39°			
CH ₃	—	Br	Br	—	—	Fluid			
CH ₃	Br	—	—	—	—	Fluid			
CH ₃	Br	—	Br	—	Br	Fluid			
CH ₃	Br	—	—	Br	—	M. p. 52—53°			
CH ₃	Br	Br	Br	Br	—	M. p. 88—89°			
CH ₃	—	Br	Br	—	—	M. p. 111° 2'—112°			
CH ₃	Br	—	Br	—	—	M. p. 44° 4'—44° 7'			
CH ₃	Br	Br	Br	—	Br	M. p. 58—59°			
CH ₃	Br	—	—	—	Br	M. p. 66°			
CH ₃	Br	—	Br	—	Br	M. p. 106° 8'—108°			
CH ₃	Br	Br	Br	—	Br	M. p. 116—117°			
CH ₃	—	Br	Br	Br	Br	M. p. 111—111° 5'			
CH ₃	Br	Br	Br	Br	Br	M. p. 283—285°			

In the first place, as to the diazoperbromide reaction for the substitution of bromine for the amido-group. We have always proceeded thus: first taking the toluidine, we have treated it with a mixture of about two volumes of nitric acid, sp. gr. 1360, to one of water. We have then introduced nitrous gas until the substance was nearly or completely dissolved. After filtering we have then added bromine dissolved in potassic or sodic bromide. After filtering out the perbromide which, in every case with which we have dealt, was precipitated either as a solid or as an oil quickly becoming so, and slightly washing with ether, we always decomposed it by means of glacial acetic acid at as low a temperature as was found capable of causing the decomposition. We adopted this method, as we found that absolute alcohol gave very untrustworthy results; in one case, on decomposing the perbromide of orthodiazodibromotoluene with alcohol, we got the whole simply as dibromotoluene. We also found that by *boiling* the perbromide with acetic acid we frequently caused the introduction of bromine into other places than that to which the diazo-group was connected.

It appeared to us, however, that by simply warming the acetic acid in a water-bath, just sufficiently to keep up a brisk reaction, the operation succeeded well.

The acetic acid we used was supplied by Messrs. Hopkin and Williams, and described as glacial at 60°. Some that we tried, described glacial at 50°, did not appear to us to answer so well.

For the elimination of the amido-group we generally acted thus:—The substance was first treated with a solution of nitrous gas in absolute alcohol, slightly warmed till gas was freely given off, allowed to cool, and then resaturated with nitrous gas, this being repeated until no considerable amount of gas was evolved on heating.

To dry the nitrous gas we used sulphuric acid kept warm in a water-bath to prevent the chamber crystals formed from becoming sufficiently solid to stop the passage of the gas.

We found the use of calcium chloride to be attended with grave objections, in some instances producing chlorinated compounds in the substances submitted to the action of the nitrous gas.

For reduction of the nitro-group tin and hydrochloric acid were mostly used. Here, however, we found it to be necessary not to use the hydrochloric acid too strong, as some substances, metanitrotoluene for example, were acted upon in such a way as to produce a chlorotoluidine instead of the substance desired. Sometimes we found iron and acetic acid to act better.

To form the dibromobenzoic acids where a mixture of chromic and acetic acids was not available, we used a mixture of 1 vol. nitric acid, sp. gr. 1360, to 3 vols. of water; sometimes boiling the dibromo-

toluene simply in a retort with a condenser, but more often heating it in a sealed tube to whatever temperature was found necessary.

To form acetyl-compounds we always found it sufficient to heat the amido-compound for at the most two or three days with the strongest acetic acid (glacial at 60°), never finding it necessary to use acetyl chloride or acetic anhydride.

In order to purify amido-compounds whose salts were decomposed by water, from any unchanged nitro-compound which might accompany them, the substance obtained by distilling with water was dissolved in ether, and precipitated with hydrochloric or sulphuric acid. The ether was then poured off, and the residue washed once or twice with ether, the salt being finally decomposed with sodic carbonate.

We wish to take this opportunity of expressing our sense of the care and diligence with which Mr. F. W. Streatfield has carried out the innumerable bromine-determinations required in the above research.

XXX.—*On the Lecture-Illustration of Chemical Curves.*

By EDMUND J. MILLS, D.Sc., F.R.S.

IN giving an account to students of the course of chemical processes, it is always advisable, and in many cases possible, to illustrate by drawings or by models of appropriate curves the intimate nature of complete experimental transactions. A teacher's exposition gains greatly in clearness by such aids, and it is seldom that he can do more than this for the dynamics of his subject. So difficult, however, is it for some minds to grasp even moderately abstract conceptions, that I have been led to contrive an apparatus suitable to a small number of useful cases, and extremely concrete in its effect; an apparatus in which the chemical process constructs its own curve under the very eyes of the observer.

As will be seen from Fig. 1, which is about one-eighteenth of the actual size, the apparatus consists of a series of glass cylinders full of water, and inverted in a corresponding series of circular glass troughs, also quite full of water; behind these is a support for an equal number of stoppered retorts, each holding about 100 c.c. The whole arrangement is virtually a system of gas-generators and pneumatic troughs. Provision is made for carrying off overflow water by cutting a deep, wide gutter all round the board on which the troughs rest, and inserting in this two exit-pipes, which are conducted to the nearest sink. The glass cylinders should have as nearly as possible an equal width, and similar internal contour at their closed ends. The frame of my

apparatus is 114 inches (289 cm.) long, and 20 inches (51 cm.) high. The cylinders have a capacity of about 270 c.c.

Action of Zinc upon Aqueous Hydric Sulphate.

Some ordinary sheet zinc, .55 mm. thick, and free from blisters, was carefully ruled with a fine needle-point into equal areas, 14 mm. square; these were cut apart with a sharp pair of scissors, an operation which admits of being very exactly performed. Purified oil of vitriol of sp. gr. 1.843, was now variously diluted to strengths progressively increasing by 3 per cent. by volume; 50 c.c. of these mixtures were placed in consecutive order in their retorts, which were then inserted in their proper positions and allowed to stand until next morning. Great attention was bestowed upon cleaning the retorts for these experiments, it being well known that the evolution of hydrogen is much retarded by the presence of even a little grease. The zincs, after rinsing in weak caustic soda and water, were immersed in strong oil of vitriol, and allowed to stand for ten minutes; they were then suddenly plunged in a rapid stream of water, and afterwards transferred to the retorts with a pair of tongs, whose ends had been previously cleaned by ignition. The stoppers, which had been well smeared beforehand with lard, were

TABLE I.

Quantity.*			Time.		
No. of Experiment.	Oil of vitriol per cent.	Millimeters of hydrogen.	Oil of vitriol per cent.	Minutes.	Millimeters of hydrogen.
1.....	3	11	27	1	0.0
2.....	6	26	"	2	2.7
3.....	9	41	"	3	5.2
4.....	12	85	"	4	11.9
5.....	15	115	"	5	18.0
6.....	18	170	"	6	30.7
7.....	21	215	"	7	51.7
8.....	24	255	"	8	68.5
9.....	27	275	"	9	87.6
10.....	30	267	"	10	126.4
11.....	33	237	"	11	162.9
12.....	36	267	"	12	198.9
13.....	39	116	"	13	228.8
14.....	42	68	"	14†	264.1
15.....	45	0			
16.....	48	0			
Initial Temp.	of liquid.	5.8°			6.6°

* Constant time for each experiment, 15½ minutes.

† After this, the surface of the zinc diminished.

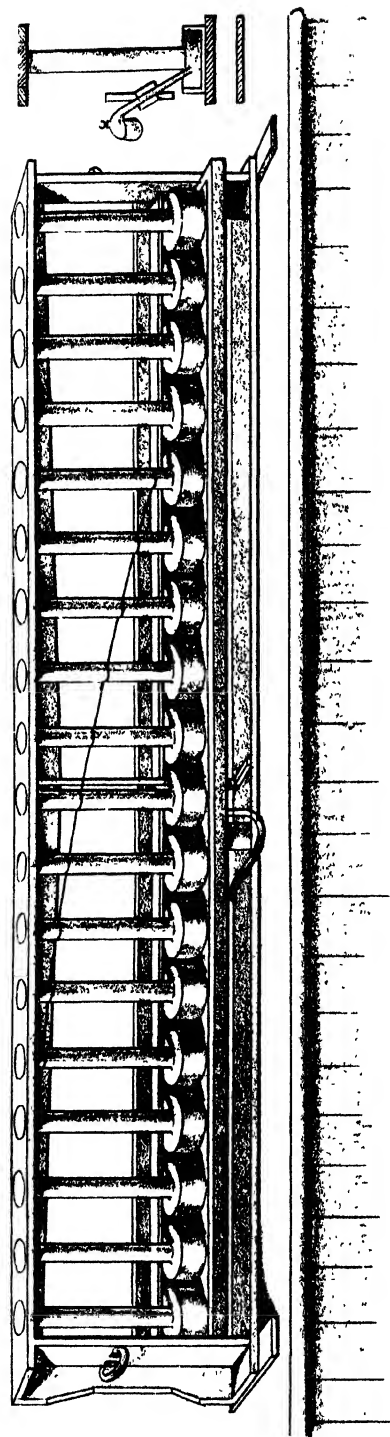


Fig. 1. Scale $\frac{1}{18}$.

Patented June 1st, 1880. M. J. L. L. L.

introduced into the retorts immediately after the zincs. The evolved hydrogen was collected in the cylinders, as long as the area of the dissolving zinc remained visibly constant.

The best form for the zincs was found to be that of a slit cylinder, readily obtained by bending them round a suitable piece of glass rod.

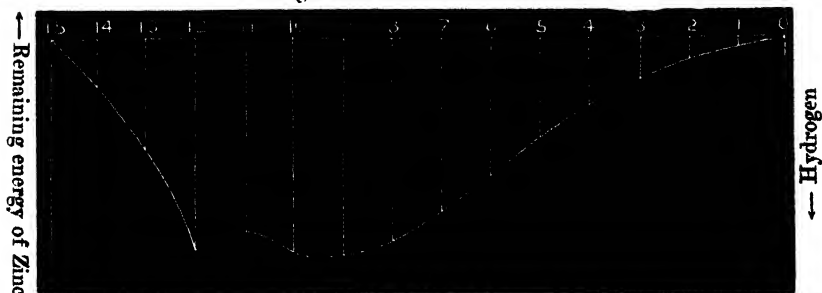
In experiments of this description, we may either trace the effect of increasing the mass of oil of vitriol, or observe the consequence of merely changing the time of contact. The result in the former case will be a quantity-curve; in the latter, a time-curve. The collection of hydrogen from a retort is arrested at any given moment by withdrawing the stopper. The numbers from a quantity-curve and time-curve are given in Table I; in the latter case the depth of the hydrogen in millimeters is reduced to a cylinder of uniform diameter (32 mm.). This time curve is indicated in Fig. I.

The exhibition of the quantity-curve requires about half an hour, and a single operator.

These experiments give ocular evidence of the following points:—As regards *quantity* (1), the progress of the reaction, if finally measured, is not according to the rule-of-three principle, but is represented by curved lines; (2), there is a maximum effect* with 27 per cent. of oil of vitriol, a minimum* with 33 per cent., and a second maximum* with 36 per cent., very weak and very strong solutions being without effect; (3) the effect of weakening is more rapid than of an equal strengthening of the solution; (4) the entire process is accomplished in three stages, represented by three curves; (5) the weight of zinc having been originally adjusted so as to fill an average cylinder with hydrogen, the water remaining in any given cylinder represents the then remaining chemical energy of the zinc. As regards *time* (1), there is but a single curve.

The following figure, drawn as a black-board illustration of the quantity-curve, should now render perfectly intelligible to the student the use and meaning of ordinates :—

Fig. 2.—HYDRIC SULPHATE.



* These are verified observations.

Action of Aluminium upon Aqueous Sodium Hydrate.

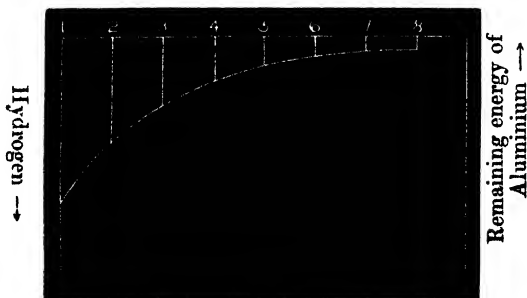
The aluminium employed in this experiment was commercial foil, each piece being 37.9 by 50.6 mm., and having a thickness of 0.0404 mm. The solution of sodic hydrate was prepared by dissolving 45 grams in water to 100 c.c.; of this, the first retort contained 34 c.c. made up to 50; the second, 30 c.c. made up to 50; and so on. The aluminium was inserted in each retort in eight equal pieces before the sodic hydrate. The results of the reaction are comprised in Table II.

TABLE II.—*Quantity-Curves.*

No of Experiment.	Cubic centimeters sodium hydrate per cent.	Millimeters of hydrogen.
1	68	201.3
2	60	131.9
3	52	87.9
4	44	55.3
5	36	39.5
6	28	27.7
7	20	19.9
8	12	15.3
Initial temperature of liquid.		6.8°

This curve is represented in Fig. 3, which would correspond with the black board illustration. The actual duration of Experiment 1 was about 40 minutes, and the interval between each successive pair of retorts less than one minute.

Fig. 3.—SODIC HYDRATE.

*Remarks.*

The numbers obtained in the above experiments are subject to some obvious sources of error. Thus, for example, most of the volumes are

observed at unequal pressures; and, as is well known, the action in each retort varies rateably from beginning to end of its course. Moreover, the more strongly acidified solutions give out much heat while reacting, being thus under a condition differing from that of the weaker solutions, which remain relatively cool. If, however, the errors of the first order of differences are not excessively large, the eye will fail to appreciate them; and thus, if care be taken, a sufficiently accurate general impression will be conveyed as to the course of a chemical change. Of the curves mentioned in this paper, the time-curve representing the action of hydric sulphate on zinc, and the quantity-curve for aluminium with sodic hydrate, are the most easily managed and give the best results. A string or straight-edge should be at hand to be laid on the two extremities of the curves, so as to show their non-linear character.

The quantity-curve usually consists of one or more consecutive hyperbolas; the time-curve is usually of a logarithmic or compound interest character.

Of other reagents tried, aqueous hydric chloride does not seem to be so manageable as the sulphate. The powerful retarding action of glycerin, or inverted sugar, or zinc chloride, on the evolution of hydrogen can readily be shown with a pair of cylinders; the accelerating effect of sodic chloride can be similarly demonstrated. The chief secret of success seems to be a low initial temperature.

My thanks are due to my lecture-assistant, Mr. Bicket, for his aid in making these experiments.

XXXI.—*On the Analysis of Organic Bodies containing Nitrogen (continued).*

By W. H. PERKIN, F.R.S.

IN the short account of my experiments on this subject recently brought before the Society, it will be remembered that it was proposed to absorb the oxide of nitrogen formed during the combustions of nitrogenous organic bodies by potassic chromate, instead of decomposing them by metallic copper as is usually done. In the analysis of uric acid, &c., then referred to, the substances were burnt from a boat with air and cupric oxide, oxygen being employed towards the finish, and the only modification of the ordinary procedure was, that potassic chromate occupied the place of reduced copper in the front part of the tube. By this method, however, a considerable quantity of reduced

copper is formed during the combustion, which would decompose more or less of the oxides of nitrogen formed, and it was therefore thought desirable to put the process to a more severe test by using plumbic chromate in place of cupric oxide; and on making combustion of uric acid in this way, it was found that the potassic chromate was not capable of completely absorbing the red fumes formed. This, result being unsatisfactory, fresh experiments were made to obtain a more powerful absorbent for these products.

Several other chromates were experimented with, and of these the most effectual was sodic chromate; this is probably due to the porous nature of the dried salt, but although more active than the potassic salt, it did not act so well as could be desired.

From the observation of a number of experiments, it appeared that some of the oxides of nitrogen present in red fumes were more easily absorbed than others. It was thought therefore that, if they could be more fully oxidised, the chromate would perhaps absorb them more freely. To accomplish this, the use of a peroxide suggested itself, such as that of lead; this, however, has the disadvantage of being easily decomposed when heated. Precipitated manganic oxide was therefore tried. The substance absorbs the oxides of nitrogen freely, but gives them up very easily when heated, and therefore would be useless alone. This, of course, was to be expected, as nitrate of manganese decomposes below 160°C . A quantity of precipitated manganic oxide was therefore made into a paste with a saturated solution of potassic chromate, and then dried and heated somewhat strongly to drive off most of the water of hydration from the manganic oxide.

To test the value of this mixture, it was placed in a short combustion tube, heated in a combustion furnace and dried air passed over it; when dry a weighed Geissler bulb charged with concentrated sulphuric acid was attached to absorb the red fumes; these were generated by igniting weighed quantities of plumbic nitrate in the back part of the tube.

Before testing the absorbing mixture in this manner, experiments were made to determine the quantity of oxides of nitrogen absorbable by sulphuric acid, which nitrate of lead would give off when heated. The following results were obtained:—

I	28.0 p. c.
II	25.8 „
III	26.8 „

In some experiments potash-bulbs were connected with the sulphuric acid bulbs, but they increased in weight only to a very minute extent.

In the following experiments about 0.2 gram of nitrate of lead was used.

The mixture of manganic oxide and potassic chromate was first tried at a temperature approaching dull redness, but in this case a certain amount of the oxides of nitrogen escaped absorption. It was observed, however, that on reducing the temperature this amount diminished, and that if the temperature were sufficiently low, all were absorbed. This will be seen from the following experiments, in which the variations between the weighings of the sulphuric acid bulbs before and after the operation are given.

I	+ 0.0002 gram
II	— 0.0001 „
III	— 0.0001 „

If no absorbing mixture had been used, the difference between the weighings would have amounted to about 0.0540 gram.

Mixtures consisting of different proportions of potassic chromate and manganic oxide have been experimented with, and in I it consisted of one part of potassic chromate and two parts of manganic oxide, and in II and III two parts of potassic chromate and one of manganic oxide.

The above results having been obtained, combustions were made to test this absorbing mixture more fully, chromate of lead being employed so as to get the maximum amount of red fumes; and as bodies containing the group NO_2 are usually supposed to yield these in larger quantities than other nitrogenous substances, dinitrobenzene was selected for analysis. About 40 or 50 grams of a specimen of this substance were fused so that a homogeneous product might be obtained. But before analysing it by the new process, four combustions of it were made by the ordinary method to determine its composition, oxide of copper and reduced copper being used. The average of these gave—

		Theory.
Carbon	42.95	42.85
Hydrogen	2.52	2.38

The slight excess of carbon is supposed to be due to the presence of a little dinitrotoluene.

In the first combustion of this product by the new process only a short length of about four inches of the absorbing mixture was used, and in this case a small quantity of red fumes escaped and was absorbed in the sulphuric acid bulbs; this caused the hydrogen determination to come .33 per cent. too high: the numbers obtained were C 42.74, H 2.71. This slight error is believed to be due to the com-

bustion being conducted too quickly. In the following, however, the length of the absorbing mixture was increased to six inches, and it will be seen that the results agree very closely with the average obtained by the old process.

	I.	II.	Average by old process.
Carbon	42.93	42.81	42.95
Hydrogen	2.54	2.48	2.52

A combustion of a less highly nitrogenised body, chromate of lead, being used as in the above, gave the following numbers. The substance was ethylorthotoluidine.*

		Theory.
Carbon	79.93	80.0
Hydrogen	9.78	9.63

These results, therefore, show that the mixture of potassic chromate and manganic oxide is effectual in absorbing the oxides of nitrogen found in the combustion of nitrogenous organic bodies.

In the preparation of the absorbing mixture, I have used potassic chromate with about ten per cent. of dichromate instead of the pure salt, because precipitated manganic oxide contains potash if this reagent has been used in this preparation, and when purchasing this article one does not know how it has been made. Ordinary powdered pyrolusite washed with dilute nitric acid was not found to answer so well as the precipitated oxide.

In making combustion by this process, a length of from four to six inches of the absorbing mixture placed in the front part of the tube has generally been used. During the preliminary process of drying with air, it has usually been heated as strongly or nearly so as the other parts of the tubes containing the cupric oxide or plumbic chromate, but before commencing the combustion the absorbing mixture must be cooled down, and only about one-fourth of the burners kept lit, and these half-turned down;† by this means a temperature of about 200—250° C. is maintained. Before detaching the bulbs every alternate burner may be used half-turned down for a few minutes, but this is scarcely necessary.

To prepare for a second combustion all the gas is turned up, as for the preliminary drying, and a current of air passed. This will cause any oxides of nitrogen which are not capable of being retained

* This substance was prepared from its acetylic derivative by my assistant, Mr. F. W. Toms, who is investigating the substitution derivatives of orthotoluidine.

† The furnace used in the above experiment was an ordinary one, consisting of a row of Bunsen's burners about three-quarters of an inch apart, the combustion tube being supported in a sheet-iron trough.

by the absorbing mixture at a high temperature to be removed; the gas is then turned down for the combustion.

The absorbing mixture of potassic chromate and manganic oxide can be used many times in succession. It has been used seven times running in my laboratory without apparently losing its power of combining with oxides of nitrogen. It therefore appears to be a very desirable substitute for freshly reduced copper.

Sulphuric and sulphurous acids are also absorbed by this mixture, but a higher temperature is required than that suitable for the absorption of red fumes; in burning, therefore, with oxide of copper, a substance containing both nitrogen and sulphur, it would be advisable to use a greater length of the absorbing mixture than above recommended, and to keep the back part of it somewhat strongly heated for the absorption of sulphurous acid, and the front part cooler for the absorption of the oxides of nitrogen.

XXXII.—On Polysulphides of Sodium. Part I. Sodium Pentasulphide.

By H. CHAPMAN JONES.

THESE compounds are generally stated to be similar to the analogous potassium compounds, but they certainly differ in some respects from potassium polysulphides, accepting their reactions as recorded. The constitution of ultramarine also points to some essential differences between these potassium and sodium compounds.

In the course of some experiments on sulphocarbonates I obtained a green substance, containing apparently sodium and sulphur (to the extent of 97 per cent.) in the proportion of 2 atoms to 4 atoms. This body is soluble in water or alcohol, has considerable tinctorial power, forms dark green solutions, which give an absorption-band, by means of which a small quantity is recognisable. It has been produced in subsequent work three or four times, and seems likely to be an oxidation product. I hope shortly to be able to make a satisfactory investigation of it.

Methods of Analysis.—The analyses of the sulphides produced have generally been made from their solutions for reasons stated below, the proportion being referred to the total sodium present, which was determined as sulphate. A freshly prepared aqueous solution can contain only sulphide and sulphate, an alcoholic solution only sulphide.

Total sulphur was estimated by oxidation with potassic permanganate in caustic soda solution. The soda used was that sold as pure from sodium. The sulphur in the potassic permanganate was estimated and allowed for. Two samples contained respectively 0.1 and 0.066 per cent. sulphur.

A measured quantity of the solution for analysis was run straight into the soda dissolved in a little water, and the mixture warmed gently if alcohol was present, till the most of it had volatilised. Not the slightest escape of SH_2 could be detected during this warming. Potassic permanganate was then added (in weighed quantity) till the liquid retained a green tint, then excess of hydrochloric acid. After heating till complete solution had taken place and the chlorine was driven off, the solution was diluted, filtered if necessary, and precipitated with barium chloride.

The sulphate present was determined by introducing the measured quantity into excess of dilute hydrochloric acid, nearly boiling; heating till SH_2 ceased to be evolved, filtering and precipitating.

By means of cadmium carbonate the polysulphide may be removed completely from aqueous solutions. Its action is described below. The cadmium carbonate used was prepared from cadmium chloride by precipitation with ammoniacal sesquicarbonate in hot solutions. The thoroughly washed dense precipitate gave on analysis 0.4336 gram CO_2 , combined with the CdO equivalent to 2.078 grams CdSO_4 , which gives the proportion of 101 CdO to 100 CO_2 . It is therefore normal carbonate.

Preparation of Sulphides.—The sulphides mentioned in this paper were prepared, unless otherwise stated, by direct union of sodium and sulphur. These products are, however, never pure, not being completely soluble in water or alcohol. The insoluble part is invariably chiefly sulphur: sometimes gray, from the presence of a black substance (see *Chem. News*); often blue, from an insoluble blue compound which turns white on exposure to the air for a few hours.

On adding sodium to melted sulphur violent deflagration takes place, the compound produced sinks as hard masses, which do not fuse till heated to a temperature at which the sulphur thickens.

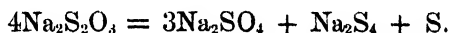
Some sulphide so prepared was broken up and remelted, then broken in pieces and analysed with the following results:—One piece, weighing 0.2676 gram, gave by ignition with H_2SO_4 0.1196 gram $\text{Na}_2\text{SO}_4 = 14.47$ per cent. sodium. Another piece, weighing 0.5080 gram, gave 0.4048 $\text{Na}_2\text{SO}_4 = 25.81$ per cent. sodium, showing a great want of homogeneity. The remainder of the stuff was extracted with water, and the solution gave, by estimation of total sodium and sulphur and sulphur as sulphate, the formula for the sulphide as $\text{Na}_2\text{S}_{4.2}$.

Another similar preparation, but not remelted, gave by analysis of its alcoholic solution the formula $\text{Na}_2\text{S}_{4.1}$, and a third preparation, in making which a great excess of sulphur was used and alcohol as the solvent, gave the formula $\text{Na}_2\text{S}_{6.2}$. A repetition of this analysis on a stronger solution gave exactly the same formula, and its solution when added to water caused precipitation of sulphur, which proves the sulphur to be in excess of that required to form Na_2S_5 .

A fourth sample was prepared more carefully, the heating being continued till the sulphur boiled, and the mass kept at that temperature for some minutes. Of this stuff two pieces, weighing 0.3995 gram, gave 0.2975 gram $\text{Na}_2\text{SO}_4 = 24.1$ per cent. Na; and one piece, weighing 0.2679 gram, gave 0.1993 gram $\text{Na}_2\text{SO}_4 = 24.1$ per cent. Na.

To ascertain approximately the behaviour of Na_2S_5 on heating, some of this sulphide was introduced with excess of sulphur in a small retort and then heated till no more sulphur distilled from it, and the sulphide fused quietly at a red heat. Of this product 0.1701 gram gave 0.1457 gram $\text{Na}_2\text{SO}_4 = 27.7$ per cent. Na. This increase of sodium by ignition from 24.1 to 27.7 per cent. is about equal to that required for the change of Na_2S_5 (22.3) to Na_2S_4 (26.4). The analysis and physical properties of an alcoholic extract of some of the above sulphide confirmed its formula as approximately Na_2S_4 .

These experiments show that Na_2S_5 on being heated gives off sulphur and leaves Na_2S_4 ; and this result is borne out by the fact that sodium thiosulphate invariably gives off sulphur when ignited, probably thus:—



This action of heat on Na_2S_5 explains the difficulty of preparing it, as the fused sulphide, where not in contact with the sulphur, would have a tendency to form Na_2S_4 .

It is stated that any lower sulphide of potassium mixed with excess of sulphide, and heated till no more sulphur is evolved, produces K_2S_5 .

In making the alcoholic solution of the ignited sulphide above there was obtained a small quantity of an apparently black residue, quite insoluble in the alcohol, but readily soluble in water, forming a fine green solution. The colour was of a purer tint than that obtained in any other case, and its absorption spectrum contained the band referred to above, but much more clearly defined. In a few hours the colour had entirely disappeared, sulphur being precipitated.

As these sulphides in the solid state are, as just shown, never pure, the result obtained by working with them can be only approximate. It was therefore deemed advisable not to spend any further time on them.

Experiments to Prepare Solutions containing the Maximum of Sulphur to the Sodium present.

The following table shows the results of the analyses of the products obtained, 5 c.c. of solution being used in each case:—

	1.	2.		3.
Na_2SO_4	·1000	·0579	·0561	·1497
BaSO_4 total	1·0869	·6969	·6751	1·1839
BaSO_4 for sulphate present	—	—	—	·0190
Formula equivalent to above	$\text{Na}_2\text{S}_{6\cdot6}$	$\text{Na}_2\text{S}_{7\cdot34}$	$\text{Na}_2\text{S}_{7\cdot32}$	$\text{Na}_2\text{S}_{5\cdot14}$

Nos. 1 and 2 were alcoholic solutions prepared by igniting sodium thiosulphate to complete decomposition, exhausting, adding much powdered sulphur, and setting aside—1, for fifteen days; 2, for five months. Both these solutions gave a precipitate of sulphur on adding water. No. 3 was prepared by deflagrating sodium in sulphur, as detailed above, extracting with water, and leaving the solution in contact with a great excess of sulphur for more than five months before filtering.

Preparation of Highest Sulphide, avoiding Excess of Sulphur.—These preparations were all made by the direct union of sodium and sulphur, using the precautions shown to be necessary by the previous work, in order to ensure the maximum amount of combined sulphur. The solutions were made from the fused solid compound, freed from adhering sulphur, then filtered as rapidly as possible.

The following table shows the results of analyses, with the formulæ deduced therefrom, 5 c.c. of solution being used for each determination:—

	1.		2.	3.	4.
Na_2SO_4	·2049	·2053	·0870	·3927	·1305
BaSO_4 total	1·5741	1·5689	·6585	2·9540	1·3522
BaSO_4 , equivalent to sulphate present ..	·0190	·0223	·0185	·0420	—
Formula	$\text{Na}_2\text{S}_{4\cdot94}$	$\text{Na}_2\text{S}_{4\cdot95}$	$\text{Na}_2\text{S}_{5\cdot14}$	$\text{Na}_2\text{S}_{4\cdot34}$	$\text{Na}_2\text{S}_{6\cdot3}$

Numbers 1, 2, and 3 were aqueous preparations, and show a very fair approximation to the formula Na_2S_6 , but No. 4, which was alcoholic; and the alcoholic ones referred to before are very wide of the mark.

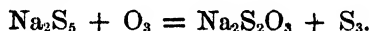
To determine whether the excess of sulphur found, when alcohol

was used as a solvent, was combined or merely dissolved, I made the following experiment:—5 c.c. of the solution containing sodium and sulphur in the proportion required by the formula $\text{Na}_2\text{S}_{7.33}$ was introduced into a tube and connected with a Sprengel pump. (The leakage in an ordinary air-pump is sufficient to completely oxidise these sulphides during their evaporation over H_2SO_4 .) The pump was worked continuously for 72 hours, the last 18 hours producing no apparent alteration. The tube was then sealed off and examined under an 1" obj. There were plenty of light yellow octahedral crystals, evidently sulphur, and the sulphide itself appeared as a thick mass, quite amorphous, not quite dry, but without the least disposition to flow.

Two months after the tube was re-examined and its contents did not show any alteration; it was therefore opened and the residue exhausted with alcohol, and the extract filtered as rapidly as possible from the sulphur crystals. The solution gave no precipitate of sulphur on adding it to water, and therefore probably did not contain more sulphur than equivalent to $\text{Na}_2\text{S}_{5.14}$, according to a previous experiment. Portions of 10 c.c. gave 0.0088 gram Na_2SO_4 and 0.0764 gram $\text{BaSO}_4 = \text{Na}_2\text{S}_{5.28}$.

The evidence detailed above seems quite conclusive that the highest sulphide of sodium has the formula Na_2S_5 , and that when a larger proportion of sulphur is obtained the excess is merely dissolved.

Atmospheric Oxidation of Sodium Pentasulphide.—Sodium pentasulphide absorbs oxygen from the air with extreme avidity, but apparently only according to the equation—



In alcoholic solutions $\text{Na}_2\text{S}_2\text{O}_3$ alone crystallises out, and may be readily redissolved by adding a small quantity of water. In aqueous solutions the sulphur alone separates.

An alcoholic solution was evaporated over strong sulphuric acid with the aid of an ordinary air-pump; in two days it was dry, but the leakage had supplied sufficient oxygen for the above reaction. Its deliquescent nature was so marked that it only dried as it oxidised. The residue contained nothing but crystals of sulphur and sodium thiosulphate, not a trace of sulphate.

Action of Water on Sodium Pentasulphide.—An aqueous solution of Na_2S_5 evolves SH_2 on gently warming. This, and the fact that sulphur is soluble to a very large extent in aqueous solution of Na_2S_5 , show that the preparation of the pentasulphide, as sometimes recommended, by boiling a lower sulphide with excess of sulphur, must be in the highest degree unsatisfactory.

By boiling with water we ought to obtain a precipitation of merely

dissolved sulphur, but I have never observed the slightest tendency to precipitate sulphur by the boiling of the aqueous solutions mentioned above. This fact affords additional evidence that all the sulphur in Na_2S_5 is really combined.

A portion of the solution which gave on analysis the formula $\text{Na}_2\text{S}_{5.14}$ was boiled for 13 hours, boiling water being added to replace that lost by evaporation. The solution was still slightly yellow while hot, but became colourless when cold. It gave qualitatively the reactions for only sulphate and thiosulphate. On analysis it yielded the following proportions:—0.0739 gram Na_2SO_4 , 0.2353 gram BaSO_4 , and 0.0360 gram BaSO_4 for sulphate present, which gives 1 atom Na to 1.16 atom S for the proportion of these elements in the thiosulphate. A comparison of the sulphate present before and after boiling shows that for each molecule of Na_2SO_4 produced there were 4.2 molecules of $\text{Na}_2\text{S}_2\text{O}_3$.

The chief action taking place here, namely, $\text{Na}_2\text{S}_5 + 3\text{OH}_2 = \text{Na}_2\text{S}_2\text{O}_3 + 3\text{SH}_2$, might produce the bodies $\text{Na}_2\text{S}_4\text{O}$ and $\text{Na}_2\text{S}_3\text{O}_2$ as intermediate products; and to ascertain if this was so, and whether the sulphate produced is a constant quantity, the following experiments were made:—

The aqueous solution of the stuff giving by analysis the formula $\text{Na}_2\text{S}_{4.84}$ was boiled for $9\frac{1}{2}$ hours with very careful exclusion of air. A part was then withdrawn for analysis and the remainder boiled for $10\frac{1}{2}$ hours more.

The first part was precipitated by cadmium carbonate, and the filtrate gave the reactions for carbonate, sulphate, and thiosulphate. It gave the following proportions on analysis:—0.1470 gram Na_2SO_4 , 0.2191 gram BaSO_4 , 0.0300 gram BaSO_4 , for sulphate (repeated and confirmed), and 0.1251 gram BaSO_4 , equivalent to the carbonate. Deducting for carbonate and sulphate, we get sodium to sulphur (in atoms) as 1 : 1.04, evidently therefore only thiosulphate, as the qualitative tests show.

The portion boiled for 20 hours contained still much sulphide, and gave on analysis 0.1279 gram Na_2SO_4 (a repetition gave exactly the same figure), 0.5050 gram BaSO_4 , and 0.0222 (repeated gave 0.0235) gram BaSO_4 for sulphate present. An equal part precipitated by cadmium carbonate, and the total sulphur in the filtrate determined gave 0.3653 gram BaSO_4 for sulphur other than sulphide. These results give the formula of the sulphide present as $\text{Na}_2\text{SO}_{4.3}$, but the use of cadmium carbonate, as shown below, tends to reduce the apparent sulphur as sulphide.

From the above data we find there has been produced 1 molecule of sulphate to 19 molecules of thiosulphate, a much smaller proportion than in the previous experiment (1 : 4.2).

The original solution (1), the portion boiled for $9\frac{1}{2}$ hours (2), and the part boiled for 20 hours (3), were then precipitated with cadmium carbonate. The precipitates gave the following results on analysis:—

	1.	2.	3.
Cd.....	43·1.43·2*	44·6	41·1
S	53·1	53·5	53·3
Formulae	$\text{CdS}_{4.32}$	$\text{CdS}_{4.2}$	$\text{CdS}_{4.5}$

These formulæ have probably all too little sulphur, as explained below, but they corroborate the evidence given by the analysis of the solutions that the change from Na_2S_5 to $\text{Na}_2\text{S}_2\text{O}_3$ by boiling with water is direct, or at least that intermediate compounds if formed are not detectable by these methods.

Action of Cadmium Carbonate on Na_2S_5 .—A neutral solution of a cadmium salt gives with sodium pentasulphide a precipitate which dissolves at once as it sinks through the alkaline solution. An excess of the cadmium salt forms at once a permanent precipitate. But if the cadmium salt is added till the precipitate first produced dissolves only slowly, the solution will in a few minutes spontaneously deposit a highly gelatinous precipitate, so that with the concentrations generally employed by me the liquid becomes converted into an unfilterable jelly.

Cadmium carbonate acts in a similar way. It is slowly converted into sulphide, which is at first redissolved in the alkaline persulphide, and if the solution is filtered in this stage a gelatinous precipitate separates from the filtrate as before.

Considerable time is therefore necessary to ensure the complete separation of all the sulphide. The precipitate so formed is, after drying at 100°C ., most certainly CdS + excess of sulphur, all the excess of sulphur being readily removable by carbon disulphide. Moreover, by digesting the gelatinous precipitate, undried, with carbon disulphide for two or three weeks, a quantity of sulphur was dissolved by the carbon disulphide quite comparable to the amount present. These observations confirm the statement of Follenius (*Zeits. Anal. Chem.*, 1874, 411), who holds, contrary to what H. Schiff supposed, that the precipitate is merely CdS + excess of sulphur.

The proportion of sulphur, however, invariably falls short of that contained in the sulphide of sodium used, and the amount of sulphate in the solution I have always found to be increased by the precipitation. Thus a dilute solution containing 10·6 (repeated 11·19) per cent. of its sodium as sulphate gave, after removal of sulphide by cadmium carbonate, 14·3 (repeat 16·6) per cent. Another, containing 6·5 per cent. before, gave 11·1 per cent. after treatment. And a

* After further washing.

third, containing about 8 per cent., had its sulphate increased to 12.4 (repeat 11.2) per cent.

The cadmium sulphide produced in these reactions has been found to be oxidised very slowly by mere exposure to air and water.

Constitution of Na_2S_5 .—The behaviour of this body throughout is consistent with the supposition that it is the tetra-thiosulphate. The great ease with which it can be converted into the mono-thiosulphate, thence into sulphate (using the silver salt to replace the last atom of dyad sulphur), points strongly in this direction. The intermediate di- and tri-thiosulphates, although apparently not producible by the replacement of the sulphur in the tetra-thiosulphate, I still have hopes of obtaining by the oxidation of lower sulphides. It seems not unlikely that the green body mentioned at the beginning of the paper is one of these.

XXXIII.—*On the Determination of Nitric Acid as Nitric Oxide, by means of its Reaction with Ferrous Salts.* Part I.

By ROBERT WARINGTON.

In agricultural analyses it is frequently desired to determine the quantity of nitric acid in substances containing a large amount of organic matter, as for instance in soils and in vegetable products. Numerous analyses of this description being required in the laboratory at Rothamsted, a trial has been made of those methods which seemed to promise most success. The investigation of the Crum-Frankland method, in which the nitric acid is estimated as nitric oxide by mixing the nitrate with oil of vitriol and then agitating with metallic mercury, has been already communicated to the Society (*Trans. Chem. Soc.*, 1879, 375). This elegant method is extremely suitable for the determination of very small quantities of nitric acid, but unfortunately fails in the presence of any considerable amount of organic matter, the results in this case being far below the truth. I have now to describe the trials made with a second method, that originated by Th. Schloesing.

Schloesing's original method was published in 1854 (*Ann. Chim. Phys.*, 40, 479); it is described in detail by Fresenius. It will suffice here to state that air is expelled from a small flask by boiling in it the solution of nitrate to be analysed; solutions of ferrous chloride and strong hydrochloric acid are then successively brought into the flask, by dipping its delivery tube in these solutions, and allowing a

partial vacuum to form in the flask by ceasing boiling. The contents of the flask is then boiled for ten minutes, and the nitric oxide gas produced collected over mercury in a small jar containing milk of lime. The gas is next transferred to another flask, previously freed from air by the ebullition of water; pure oxygen is then admitted, and the nitric oxide converted into nitric acid, the quantity of which is determined by titration with a standard solution of alkali. Working in this manner, with quantities of nitre varying from 0.100 to 0.339 gram, he obtained from 98 to 100 per cent. of the nitric acid taken. With very small quantities of nitre the results were decidedly too low. To meet cases of this kind Schloesing devised a smaller generating apparatus, from which all air could be removed by a current of pure carbonic acid, the same gas being used to chase out the last traces of nitric oxide at the end of the operation. With this modified apparatus he obtained from 0.00516 gram of nitre 95.3 per cent. of the nitric acid present, and from the still smaller quantity of 0.00186 gram 89.9 per cent.

Schloesing made experiments with a considerable number of organic bodies; their presence had generally little or no influence on the result, which always exhibited a slight deficiency. Cane-sugar and gelatin occasioned the most striking diminution in the nitric acid found; the error could be remedied to some extent by increasing the proportion of ferrous chloride employed. He found that 0.150 gram of nitre, with 1 gram of sugar, and ferrous chloride equal to 0.5 gram of metallic iron, yielded 89.4 per cent. of the nitric acid present. The same materials, with 0.5 gram of sugar, yielded 94 per cent. Increasing the iron to 1 gram, the product was 95.8 per cent.; and further increasing it to 4 grams, 97.4 per cent. was obtained.

Schloesing's method of determining nitric acid has been largely employed both in Germany and France, but, as far as I am aware, has been but little used in England. The method has been many times examined, and various modifications have been introduced. The generating flask has been furnished with a caoutchouc stopper, carrying a supply tube as well as a delivery tube, thus allowing a series of determinations to be made without intermission, a fresh sample of nitrate being introduced as soon as the gas from the preceding sample has been collected. The gas has also been collected over a solution of caustic soda, previously boiled, instead of over mercury. This modification, due to Reichardt (*Zeits. anal. Chem.*, 1870, 24), has been largely followed. Schulze and Wulfert (*Landw. Versuchs.-Stat.*, 12, 164) have also determined the quantity of nitric oxide produced by measuring its volume, instead of converting it into nitric acid.

The results obtained by recent investigators have been quite similar to those quoted by Schloesing, and display a similar error of deficiency

whenever very small quantities of nitrate are operated on. Thus Eder (*Zeits. anal. Chem.*, 1877, 291), when collecting the nitric oxide over mercury, and subsequently converting it into nitric acid, obtained with 0.1448—0.1662 gram of nitre 98.5—99.8 per cent. of the nitric acid taken; but with 0.0279 and 0.0249 gram of nitre, only 87.5 and 89.2 per cent. of the nitric acid present was recovered. In his experiments with organic matter, 0.1599 gram of nitre, with 0.4 gram of starch, yielded 99.3 per cent. of the nitric acid taken; but with 0.0403 gram of nitre, and 0.3 gram of starch, the product was only 90.3 per cent. When, following Reichardt's plan, he collected the gas over a solution of soda, and used extreme care to exclude air, he obtained from 0.1884—0.3796 gram of nitre 98.5—99.3 per cent. of the nitric acid present, and with 0.0555 and 0.0527 gram of nitre, 93.0 and 90.1 per cent.

In making a trial of Schloesing's method at Rothamsted, the special object kept in view was to ascertain its suitability for determining very small quantities of nitric acid; only small quantities of nitre have therefore been operated on, at most 0.037 gram. For the same reason the nitric oxide produced has been determined by gas analysis, this being the most exact method for the determination of minute quantities of matter.

The apparatus first employed consisted of a flask of about 150 c.c. capacity, closed by a caoutchouc stopper carrying two tubes. The supply tube was of narrow bore, and about 16 inches in height, so as to allow of liquids being introduced during ebullition, and while the delivery tube was immersed in a trough of mercury; the supply tube terminated above in a small funnel, attached by a stout caoutchouc tube provided with a clamp. The delivery tube dipped into a trough of mercury; the tube was of some height in order to avoid any liquid being drawn back into the flask during any check in the boiling.

In using this apparatus, 40 c.c. of a solution of ferrous chloride, containing 200 grams of iron per liter, and 20 c.c. of strong hydrochloric acid, were introduced into the flask, which was then placed in a chloride of calcium bath, maintained at a temperature of 140°, by which means a vigorous ebullition was produced. As soon as the principal amount of air had been expelled, a glass jar was placed over the end of the delivery tube in the mercurial trough, and the boiling continued until 30 c.c. of liquid had distilled over, the mercury in the trough being kept sufficiently cool by a layer of water on its surface. The boiling off of 30 c.c. of hydrochloric acid proved insufficient to expel all traces of permanent gas from the flask, minute bubbles continuing to rise in the collecting jar; nor was the removal of air made more complete by introducing another 30 c.c. of hydrochloric acid

through the supply tube, and boiling off a second time. The small quantity of gas thus continually evolved was most probably due to air dissolved in the hydrochloric acid.

The air having been as far as possible expelled, the nitrate, dissolved in 10 c.c. of boiled water, was introduced through the supply tube, and rinsed down with 20 c.c. of hydrochloric acid; boiling was then continued till 30 c.c. of liquid had distilled, the gas and the distillate being collected in a jar over mercury. On the completion of one operation a fresh jar was placed over the delivery tube, and a fresh charge of nitrate and hydrochloric acid run into the generating flask, which was thus continuously employed. With the bath at 140° , one operation would take 20—30 minutes.

The gas obtained was accurately measured, and analysed by successive absorption with solution of caustic soda and solution of ferrous sulphate. These absorbents were employed because they had been made use of in similar German work; they were afterwards replaced by concentrated solutions of potash and ferrous chloride. The whole of the gas analysis was performed in Frankland's modification of Regnault's apparatus.

The use of a ferrous salt as an absorbent for nitric oxide demands a word of remark. It must always be recollected in using this absorbent that the nitric oxide is only feebly combined with the ferrous salt, and is given up again on a rise of temperature, or in a vacuum. While, therefore, good results may be obtained when a large proportion of the gas is composed of nitric oxide, the method would probably fail to remove a small quantity of nitric oxide from a large volume of other gases, in which the tension of the nitric oxide was but feeble. For the same reason a trace of nitric oxide is apt to be given up when the unabsorbed gas is removed for measurement in the eudiometer, a vacuum being necessarily applied for this purpose. In many analyses the unabsorbed gas was brought a second time in contact with a fresh quantity of ferrous sulphate, with the view of removing this source of error. After the use of ferrous chloride was adopted, this second absorption was generally omitted, the ferrous chloride being more concentrated, and more powerful in its action than the ferrous sulphate. The analyses in which the nitric oxide has been removed by two absorptions are distinguished by an asterisk. Ferrous chloride has been already employed by Wulfert (*Landw. Versuchs.-Stat.*, 1869, **12**, 170) as an absorbent for nitric oxide.

In the following table the results of the gas analysis are given for those experiments in which nitre only was employed. The gas measured at every stage of the analysis has been reckoned as nitric oxide, and reduced to its equivalent in nitrogen; the relation of the gas found to the quantity of nitrogen taken is thus at once manifest:—

TABLE I.—*Experiments with First Form of Apparatus.
Trials with Nitre only.*

No.	Material operated on.	Nitrogen taken as nitre. Milligrams.	Gas obtained expressed in mgrms. of nitrogen.			
			Total gas.	After soda.	Absorbed by ferrous sulphate.	Residue after ferrous sulphate.
1	Nitre only	5·138	5·096	—	—	—
2	"	"	5·086	—	—	—
3	"	"	5·058	—	—	—
4	"	"	5·085	5·055	4·804	0·251
5	"	"	5·095	5·073	4·879	0·194*
6	"	"	5·098	—	4·912	0·186
7	"	1·415	1·404	—	—	—
8	"	"	1·417	1·407	1·231	0·176*
9	"	0·708	0·607	0·603	0·518	0·085
10	"	"	0·603	0·599	0·494	0·105

If the total gas obtained were reckoned as nitric oxide, the average product of the first six experiments would be 99 per cent.; of Experiments 7—8, with a smaller quantity of nitre, 99·7 per cent.; and of Experiments 9—10, 85·5 per cent. In the last-named experiments a smaller volume of hydrochloric acid was introduced into the apparatus in each determination. The gas obtained was, however, in no case pure nitric oxide, and if we regard only the volume actually absorbed by ferrous sulphate, we have 94·7, 87·0, and 71·5 as the percentage products obtained in the three groups of experiments just referred to. The proportion of nitric oxide obtained thus diminishes rapidly with decreasing quantities of nitrate taken. Since, however, the small quantity of nitrogen introduced into the apparatus by the materials employed in each experiment is a fairly constant quantity, so long as the volume of these materials remains unaltered, it follows that with certain quantities of nitrate, this constant error of excess serves to correct the error of deficiency, when the *total volume* of the gas is taken as the basis of calculation.

The deficiency in the nitric oxide obtained may be due to oxygen introduced in the materials employed; to an incomplete reaction between the nitrate and ferrous salt in the generating flask; or to a formation of nitrous oxide and nitrogen as bye-products of this reaction. The first two suppositions would best explain the increasing proportional deficiency with decreasing quantities of nitrate.

The next series of experiments was made in the same apparatus; the object in view was to ascertain the effect of ammonium salts and of cane-sugar.

TABLE II.—*Experiments with First Form of Apparatus.*
Trials with Nitre, Chloride of Ammonium, and Sugar.

No.	Substances added to the nitre used.	Nitrogen taken as nitre. Mgrms.	Gas obtained expressed in mgrms. of nitrogen.				
			Total gas.	After soda.	Absorbed by FeSO_4 .	Absorbed by soda.	Residue left by FeSO_4 .
1	NH_4Cl , 0·02 gram	5·138	5·160	—	—	—	—
2	" "	"	5·151	5·127	4·939	0·024	0·188*
3	Sugar, 0·5 gram ..	"	5·166	—	—	—	—
4	" " ..	"	5·874	5·007	4·696	0·867	0·321*
5	" " ..	"	5·870	4·940	4·614	0·930	0·296*
6	" " ..	"	5·919	4·857	4·614	1·062	0·243*
7	NH_4Cl , 0·02 gram, and sugar, 1 gram	"	6·144	4·985	4·650	1·209	0·284*
8	" " "	"	6·591	4·955	4·683	1·636	0·272*
9	Sugar, 1 gram	1·415	1·630	1·350	1·129	0·280	0·221*
10	" "	"	1·656	1·347	1·154	0·269	0·233*
11	" "	"	1·668	1·366	1·140	0·302	0·226*

The presence of ammonium salts does not apparently affect the reaction; the nitrogen found as nitric oxide in Exp. 2 amounts to 96·1 per cent. of the nitrogen taken.

In the experiments with sugar it was remarked that the distillate from the generating flask was always of a brown colour, and not unfrequently this colour was very dark in tint. It was at first supposed that the caramel produced in the flask had been carried over in the form of spray; as, however, the introduction of a large bulb half filled with glass beads in the upright exit tube from the flask had no effect in diminishing the amount of colour, and as no trace of iron could be found in the distillate, it became evident that the brown colouring matter was a volatile substance produced by the oxidation of the sugar. In subsequent experiments with vegetable juices this brown colour has always been observed. The brown distillates in question have a somewhat aromatic and ethereal odour. I have not met with any reference to these brown distillates in any of the papers dealing with the method.

The gas obtained when sugar is present is much larger in volume than that obtained with a pure nitrate, and contains a considerable quantity of carbonic acid. The carbonic acid is apparently produced by the action of the nitric acid and ferric chloride on the sugar, as it is found to vary with the quantity of nitre used, as may be seen by comparing the carbonic acid in Exps. 4—8, with that given in Exps. 9—11. When a number of similar experiments are made in succession, as in the case of Exps. 3—6, the carbonic acid increases in quantity with each experiment.

The quantity of gas unabsorbed either by soda or ferrous salt, is seen to be considerably increased in those experiments in which sugar was present. This increase is apparently due to the presence of carbonic oxide. The residual gas from Exps. 10 and 11 was mixed and treated with solution of cuprous chloride; the mixed gas was equal to 0.454 mgrm. of nitrogen, after absorption it equalled only 0.267 mgrm.; about two-fifths of the gas was thus carbonic oxide.

The influence of the sugar on the quantity of nitric oxide obtained is clearly to reduce its amount, as already shown by Schloesing and other experimenters. The average product of Exps. 4—8 is 90.6 per cent. of the nitrogen taken, as compared with 95—96 per cent. obtained without sugar. With the smaller quantity of nitre employed in Exps. 9—11 the product with sugar is only 80.6 per cent.

At this stage of the investigation a number of determinations of the nitrates present in the sap of mangel wurzel roots were made in the laboratory, the apparatus used for the above experiments being employed. 20 grams of the sap were concentrated with lime-water, then treated with alcohol and filtered; the filtrate was then evaporated and yielded a clear and nearly colourless syrup, which was then introduced into the apparatus with 20 c.c. of hydrochloric acid. With the very large quantities both of nitrate and sugar contained in the mangel sap all the facts observed before reappeared on an exaggerated scale. The distillates were very dark in colour; the carbonic acid amounted at times to more than one-half of the total gas; the residue left after absorption with potash and ferrous chloride was more considerable, and in some cases more than two-thirds of its volume was carbonic oxide.

In these experiments with mangel sap it was observed that the gas when left all night in the jar in which it was collected diminished considerably in volume, a part of the gas being absorbed by the distillate, amounting to about 30 c.c., also present in the jar, the distillate at the same time becoming darker in tint. With the view of ascertaining whether this diminution in volume affected the nitric oxide, or merely the associated gases, some comparative experiments were made with known amounts of nitre and sugar. In some cases the gases were simply collected as before over mercury, and were left in contact with the hydrochloric distillate which accompanied them. In other cases the gas jar received at starting about 25 c.c. of a boiled and highly concentrated solution of soda, more than sufficient to neutralise all the hydrochloric acid afterwards distilled; in this way a trial was made of the German method of collecting the evolved gas over caustic alkali. The results are given in the following table:—

TABLE III.—*Experiments with First Form of Apparatus.*
Alterations in Gas by prolonged contact with the Distillate.

No.	Substances added to the nitre used.	Nitrogen taken as nitre. Mgrms.	Gas obtained expressed in mgrms. of nitrogen.				
			Total gas.	After potash.	Ab-sorbed by ferrous chloride.	Ab-sorbed by potash.	Residue left by ferrous chloride.
<i>Gas analysed same day.</i>							
1	Sugar, 1 gram . . .	5·139	6·414	4·831	4·592	1·583	0·239*
2	" " ..	"	7·113	4·988	4·554	2·125	0·434*
3	" " ..	0·708	3·780	0·832	0·610	2·948	0·222
<i>Gas analysed next day.</i>							
4	" " ..	5·139	5·666	4·673	4·423	0·993	0·250*
5	" " ..	"	6·512	4·845	4·497	1·667	0·348*
6	" " ..	0·708	2·103	0·800	0·556	1·303	0·244
<i>Gas analysed after two days.</i>							
7	" " ..	5·139	5·344	4·655	4·313	0·689	0·342*
<i>Gas collected over Soda and analysed same day.</i>							
8	Nitre only	5·141	4·971	—	4·860	—	0·111*
9	" "	0·708	0·620	—	0·534	—	0·086
10	Sugar, 1 gram . . .	5·140	4·834	—	4·514	—	0·320*
<i>Gas collected over Soda and analysed next day.</i>							
11	Nitre only	5·141	4·615	—	4·490	—	0·125*
12	" "	0·708	0·314	—	0·235	—	0·079
13	Sugar, 1 gram . . .	5·140	3·140	—	2·707	—	0·433*

Looking first at the experiments with nitre and sugar in which the gas was in contact with an acid distillate we see, by comparing Exps. 1—3 with Exps. 4—7, that the diminution in volume which occurs on standing is chiefly due to the absorption of carbonic acid; the nitric oxide is, however, also affected. Thus the nitric oxide found amounts to a product of 89·0 per cent. as the mean of Exps. 1 and 2, in which the gas was analysed two or three hours after it was obtained, and to a product of 86·8 per cent. as the result of the duplicate Exps. 4 and 5, in which the gas stood in the jar for 24 hours before analysis. In Exp. 7, in which the gas from another experiment in the same series was allowed to stand two days before analysis, the nitric oxide found is only equal to 83·9 per cent. of the nitrogen taken. When we have

to deal with much smaller volumes of nitric oxide, as in Exps. 3 and 6, the loss by absorption forms a still larger percentage error. Thus the yield of Exp. 3, in which the gas was analysed two hours after its production, is 86.2 per cent., and that of Exp. 6, in which the gas stood a day and night before analysis, is only 78.5 per cent. of the nitrogen taken. It is quite evident from these experiments that nitric oxide left in contact with the brown acid distillate suffers absorption, and that the gas should be analysed as soon as possible.

The loss of nitric oxide by absorption is still greater when the gas is collected over soda. When pure nitre was operated on, and the distillate was therefore free from organic matter, the product in the case of Exp. 8 was 94.5 per cent., and in the case of Exp. 9, where the quantity of nitre was very small, 75.4 per cent. These analyses were made about $1\frac{1}{2}$ hour after the collection of the gas, and show results similar to those yielded by the same quantities of nitre when no soda was employed. In the duplicate Exps. 11 and 12, analysed next day, the nitric oxide found amounted respectively to a product of 87.3 and 33.2 per cent.; a considerable loss had thus taken place. In another pair of experiments (Nos. 10 and 13), in which sugar was employed and the gas thus brought in contact with an alkaline organic distillate, the product was 87.8 per cent. when the gas was immediately analysed, and 52.6 per cent. after standing 24 hours.

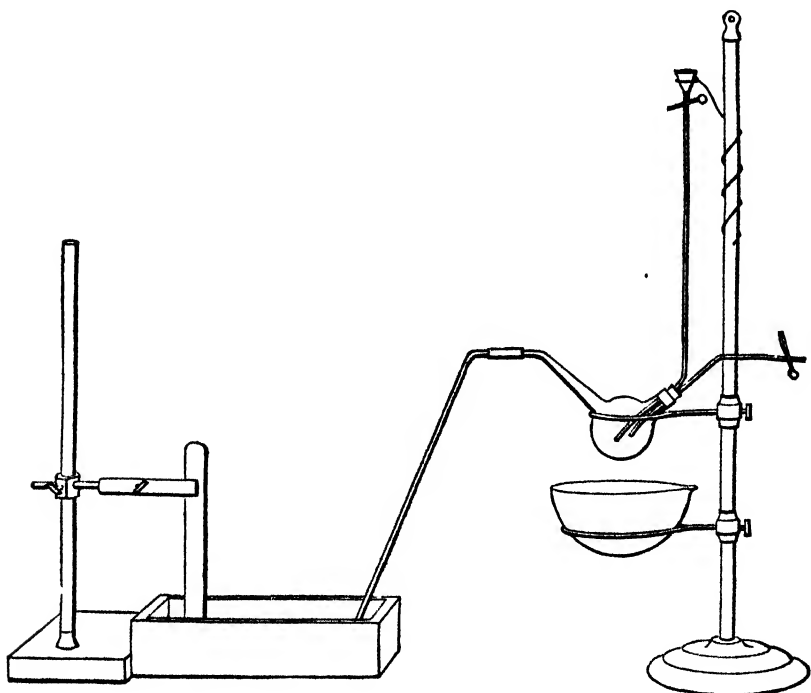
A comparative idea of the extent of loss by absorption under different circumstances will be gained by looking at the results given by one quantity of nitre (nitrogen 5.139—5.141 mgrms.) only. The nitric oxide from this quantity of nitre lost by standing 24 hours over an acid organic distillate an amount equal to 2.2 per cent. of the nitrogen taken, and by standing 48 hours it lost 5.1 per cent. When soda was employed in the absence of organic matter, the loss in 24 hours amounted to 7.2 per cent. When the gas was left for the same time in contact with an alkaline organic distillate the loss was 35.2 per cent.

Several qualitative experiments were also made, all showing a gradual absorption of nitric oxide by a solution of caustic soda. The decomposition of nitric oxide when in contact with caustic potash into nitrous acid, nitrous oxide, and free nitrogen, has been recently pointed out by Russell and Lapraik (*Chem. Soc. J.*, 1877, ii, 36), and its still more rapid decomposition by potash when pyrogallol is also present has been shown by the same authors, and also by Thomas (*ibid.*, 32). The results quoted above appear to be perfectly in accordance with their observations. It is evident therefore that if nitric oxide is collected over a solution of soda, after the method commonly employed in Germany, the gas must be measured immediately if loss is to be avoided. In the case, however, of the analysis of vegetable juices, when the distillate is necessarily contaminated with organic matter, it seems

doubtful whether the most speedy mode of working will suffice to protect the result from loss.

The results which have been now described plainly show that, even under the most favourable circumstances, the method of determination here employed failed to give accurate results when very small quantities of nitrate were taken, a trial was therefore next made of the modification recommended by Schloesing, in which carbonic acid gas is employed both to expel air from the apparatus, and to chase out the nitric oxide produced.

The form of apparatus adopted is shown by the accompanying figure. The vessel in which the reaction takes place is a small tubulated receiver, the tubulure of which has been bent near its extremity to make a convenient junction with the delivery tube, which dips into a trough of mercury on the left; the long supply tube attached to the receiver is of small bore, and is easily filled by a $\frac{1}{2}$ c.c. of liquid. The short tube to the right is also of small bore, and is connected by a caoutchouc tube and clamp with an apparatus for the continuous production of carbonic acid.



In using this apparatus the supply tube is first filled with strong hydrochloric acid, and carbonic acid is passed through the apparatus till a portion of the gas collected in a jar over mercury is found to be

entirely absorbed by caustic potash. The current of carbonic acid is then stopped by closing the clamp to the right. A chloride of calcium bath at 140° is next brought under the receiver, which is immersed one-half or more in the hot fluid; the temperature of the bath is maintained throughout the operation by a gas-burner placed beneath it. By allowing a few drops of hydrochloric acid to enter the hot receiver the carbonic acid it contains is almost entirely expelled. A jar filled with mercury is then placed over the end of the delivery tube, and all is ready for the commencement of a determination.

The nitrate, which should be in the form of a dry residue in a small beaker or bason, is dissolved in about 2 c.c.* of the ferrous chloride solution previously described, 1 c.c. of strong hydrochloric acid is added, and the whole is then introduced into the receiver through the supply tube, being followed by successive rinsings with hydrochloric acid, each rinsing not exceeding a $\frac{1}{2}$ c.c., as the object is to diminish as far as possible the bulk of liquid introduced. The contents of the receiver is in a few minutes boiled to dryness; a little carbonic acid is admitted before dryness is reached, and again afterwards to drive over all remains of nitric oxide. If the gas will not be analysed till next day it is advisable to use more carbonic acid, so as to leave the nitric oxide diluted with several times its volume of that gas. As soon as one operation is concluded the apparatus is ready for another charge.

This mode of work presents the following advantages:—1. The volume of liquid introduced into the apparatus is much diminished, and with this of course the amount of dissolved air contributed from this source. 2. By evaporation to dryness a complete reaction of the nitrate and ferrous chloride, and a perfect expulsion of the nitric oxide formed, is as far as possible attained. 3. The nitric oxide in the collecting jar is left in contact with a much smaller volume of acid distillate than before, and its liability to absorption is greatly diminished by its dilution with carbonic acid.

The results obtained with this apparatus are shown in the following table:—

* Supposing the ferrous chloride to contain 2 grams of iron per 10 c.c., then 1 c.c. of the solution will be nearly equivalent to 0.12 gram of nitre, or 0.0166 gram of nitrogen. A considerable excess of iron should, however, always be used.

TABLE IV.—*Experiments with Second Form of Apparatus.*
Nitre alone, and with Ammonium Salts and Organic Matter.

No.	Substances added to the nitre taken.	When analysed.	Nitrogen taken as nitre. Mgrms.	Gas obtained expressed as mgrms. of nitrogen.			Nitrogen found as nitric oxide for 100 taken.
				After potash.	Absorbed by ferrous chloride.	Residue left by ferrous chloride.	
1	Nothing	Same day	5·141	4·969	4·896	0·073	95·23
2	"	"	1·415	1·366	1·310	0·055	92·58
3	"	Next day	"	1·372	1·328	0·044*	93·85
4	"	Same day	0·354	0·348	0·314	0·034	88·62
5	"	Next day	"	0·344	0·313	0·031	88·53
6	Sugar, 0·5 gram..	Same day	1·415	1·395	1·307	0·088*	92·37
7	Sugar, 0·5 gram } NH ₄ Cl, 0·05 gr. }	"	"	1·429	1·324	0·104	93·57
8	NH ₄ Cl, 0·05 gram	After two days	"	1·436	1·309	0·127	92·51
9	Asparagin, 0·05 gr	Same day	"	1·368	1·331	0·037	94·06
10	" " "	Next day	"	1·360	1·324	0·036	93·57
11	Skim-milk, 5 c.c...	Same day	"	1·430	1·319	0·111	93·22

The first point to be remarked is the greater purity of the gas obtained in this mode of working; the residue left unabsorbed by potash and ferrous chloride is now much reduced in quantity, the bubble was, in fact, frequently so small as to be with difficulty manipulated.

Only a single experiment with the larger quantity of nitre is recorded; the product obtained is as good, but no better than that yielded by some of the experiments made in the former apparatus. When we come, however, to the smaller quantities of nitre, a marked improvement is apparent as compared with the earlier results. With nitre equal to 1·415 mgrm. nitrogen, we now obtain a mean product of 93·2 per cent., as against 87·0 per cent. previously obtained. With a still smaller quantity of nitre, equal to 0·354 mgrm. of nitrogen, the mean product is 88·6 per cent. of the nitrogen taken. These results are somewhat better than those obtained by Eder, already quoted, but are not quite equal to those given by Schloesing, as obtained with a similar apparatus.

In the experiments with organic matter a considerable improvement is manifest. Bearing in mind the ingredients known to occur in vegetable juices, determinations were made of nitrates in the presence of ammonium salts, asparagin, albuminoids, and sugar; none of these substances appear to have any practical influence on the result. It will be recollected that in the previous mode of working, and with the

same quantity of nitre, the percentage result fell from 87.0 to 80.6 per cent., by the addition of sugar. The product with sugar is now 93.0 per cent.

The loss of nitric oxide by standing in contact with the distillate is also now hardly perceptible, as will be seen by comparing the results obtained by an immediate analysis of the gas with those yielded by analyses made the following day.

The method here described is not well suited for the analysis of nitrites. A nitrite treated with the ferrous chloride solution is at once decomposed, and nitric oxide evolved. Nitrites must thus be introduced into the apparatus with water only, and the bulk of the liquid used thus inconveniently increased. A better plan is to convert nitrites into nitrates by means of peroxide of hydrogen solution, or by permanganate of potassium, and then proceed as already directed. Solution of peroxide of hydrogen will convert a neutral solution of potassium nitrite into nitrate in a few minutes; the excess of peroxide will, of course, be dissipated during the evaporation to dryness.

Further test experiments have not yet been made with this new form of apparatus, it being thought that other improvements could be introduced; as, however, these cannot be carried out for some time, the present results are submitted as a preliminary report.

XXXIV.—CONTRIBUTIONS FROM THE LABORATORY OF THE ROYAL COLLEGE OF CHEMISTRY.

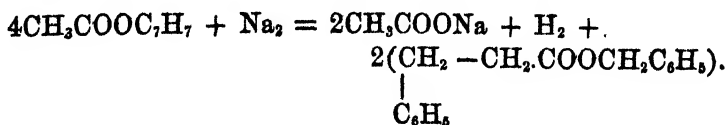
On the Action of Sodium on some Ethereal Salts of Phenylacetic Acid.

Part I.

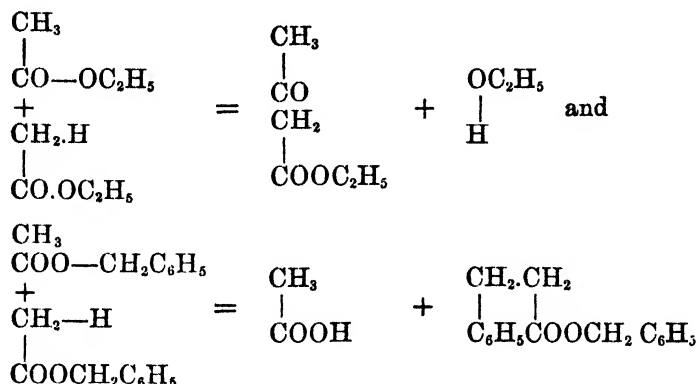
By W. R. HODGKINSON.

IN a contribution to *Liebig's Annalen*, by Max Conrad and myself (*Annalen*, 193, 298), we have shown the influence of the presence of a phenyl group in ethers of fatty acids to result in the substitution of one or more of the hydrogen atoms, and combination with the carbon immediately joined to the carboxyl group, by the group containing the phenyl, giving a synthesis of so-called aromatic fatty acids.

From benzylic acetate, $\text{CH}_3\text{COOC}_7\text{H}_7$, for instance, the benzylic ether of β -phenylpropionic acid ($\text{C}_6\text{H}_5\text{CH}_2\text{CH}_2\text{COOC}_7\text{H}_7$), was obtained as a primary product, and secondarily, by the action of sodium on this substance, dibenzylacetic and β -phenylacrylic acids, the first reaction being—

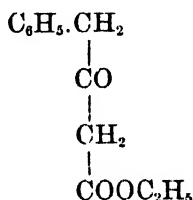


The difference between this reaction and the one by which ethylic acetoacetate is produced may perhaps be shown thus:—

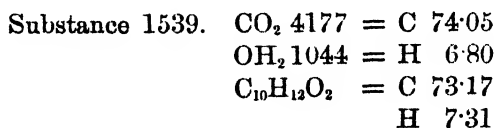


Benzyl propionate, butyrate, &c., gave analogous results.

This being the effect of a phenyl group on the *base* of the ethereal salt, it occurred to me to try if its presence in the acid or negative portion would alter the result. For this purpose α -tolnic acid seemed likely to give results, as one might expect from its ethyl ether to obtain an ethylic phenylacetoacetate,



The ether was prepared by digesting the potassic salt of the acid with ethylic iodide, and obtained as a liquid boiling at 229° (corr.) of sp. gr. 1.0861 at 16° C. (Noad, *Ann. Pharm.*, **63**, 295).



Metallic sodium acts but slightly on the substance at ordinary temperature, and only moderately when heated, hydrogen being evolved.

At first the proportion of sodium employed was approximately $\text{Na}_2.4(\text{C}_{10}\text{H}_{12}\text{O}_2)$, but with this amount all the metal could not be got to dissolve, 4 to 5 per cent. remaining unacted on.

The proper proportion and best results were obtained with 50 grams of the ether, and 2.5 sodium = $6(\text{C}_{10}\text{H}_{12}\text{O}_2) + \text{Na}_2$ nearly.

In an early experiment with upright condenser it was observed that

a considerable amount of a liquid condensed back, although the temperature in the retort was under 100° .

It was therefore arranged, by means of a shallow retort and downwards directed condenser, that the liquid should be removed as fast as formed from further contact with the metal.

In an experiment with 50 grams of the ether, nearly 10 grams of a liquid distilled over during the reaction, between 75° and 90° , and gave on analysis—

Substance 0.0790. CO_2 0.1544 = C 53.30

OH_2 0.0719 = H 10.11

Substance 0.0900. CO_2 0.1730 = C 52.43

OH_2 0.0920 = H 11.35

= C 54.54

$\text{CH}_3\text{COOC}_2\text{H}_5$ = H 9.99

On saponification with baric hydrate, barium salt analysis gave—

I. 9639 BaSO_4 8760

II. 1298 BaSO_4 1200

Theory..... $(\text{CH}_3\text{COO})_2\text{Ba} = \text{Ba}$ 53.72

Found..... I. 54.35

II. 54.31

The silver salt had all the characters of argentic acetate—

0.0717 substance giving Ag 0.0466 = 64.9 per cent.

$\text{CH}_3\text{COOAg} = \text{Ag}$ 64.66 per cent.

The residue in the retort, forming a thick mass, gave on addition of water, a solution, in which $\text{SO}_2(\text{HO})_2$ caused a white precipitate, and an oily body, which was separated and distilled.

On shaking the acidified aqueous solution with ether, an acid was obtained, crystallising from OH_2 in long needles, melting at 76° , which was identified as phenylacetic acid.

A small quantity of acetic acid was also obtained from the aqueous solution on distillation with steam.

The oily portion separated when distilled into a little unacted upon ethylic phen-acetate, and an oil boiling above 300°C ., which, after being several times fractioned in a vacuum, boils constantly at 250° under 60 mm. It has a sp. gr. 1.0628 at 20° .

Different preparations gave—

C 79.58

C 81.19

C 80.90

C 81.14

H 7.41

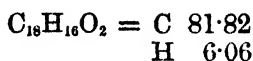
H 6.56

H 6.53

H 5.03

$\text{C}_{18}\text{H}_{20}\text{O}_2 = \text{C}$ 80.60

H 7.46

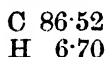


The vapour-density of the body could not be determined, as decomposition takes place a little over 360° .

Only having as yet a small amount of the substance, I have not been able to do more than saponify with potash.

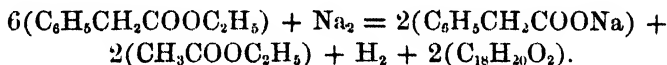
On washing and acidifying the alkaline solution, phenylacetic acid, *melting at 76°*, was alone obtained.

A residual oil on distillation in a vacuum gave a fraction between 270° and 300°, under 60 mm., giving on analysis—



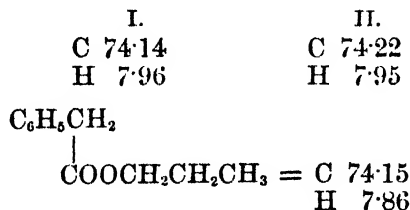
which approximates to the formula, $C_{18}H_{16}O$, and appears to be a phenol. But I must reserve this, with other bodies to be mentioned, for further investigation.

The action of sodium on ethylic phenyl-acetate, at a temperature of about 100°, and when the ethylic acetate is removed as fast as formed, appears to take place almost quantitatively, according to the equation—

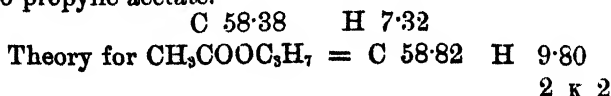


The action of the metal on other ethers of phenylacetate in the *fatty series*, appears to be quite analogous, although, owing to the higher temperatures at which the reactions take place, secondary products are formed in larger quantity.

Propylic phenyl-acetate was made by heating alcoholic solution of potassic phenyl-acetate with propylic iodide for two days. It is a pleasantly smelling liquid, of sp. gr. 1.0142 at 18°, boiling at 238° (corr.) Its purity was assured by the combustions in which was found—



On treating with sodium, action takes place with evolution of hydrogen at about 110° , a light liquid distilling over, which on rectification boils between 95° and 100° , and gives figures on analysis corresponding to propylic acetate.



On saponification and making into silver salt—

0.0349 substance gave 0.0225 Ag = 64.46 per cent.

CH_3COOAg = 64.66 per cent.

The product of the reaction treated with water, as with the ethylic phen-acetate, gives a solution containing a sodium compound and an oil.

The aqueous solution on adding $\text{SO}_2(\text{HO})_2$ gives a dense precipitate, a mixture of two bodies, phenylacetic acid easily soluble in ether, and a substance difficultly soluble therein, and separating from it in fine grouped needles. After washing with boiling water, in which it is quite insoluble, to remove phenylacetic acid, and crystallisation from petroleum, it is obtained in fine white needles melting at 170° , and giving on analysis—

I. C 80.39

H 6.02

II. C 80.31

H 5.97

$\text{C}_{24}\text{H}_{20}\text{O}_3$ = C 80.90

H 5.62

It is insoluble in acids and caustic alkalis (although strong K_2CO_3 solution dissolves it without evolution of CO_2), and almost insoluble in alcohol and ether. It has a sp. gr. of 1.039 at 17° .

The yield of this substance is very small, and appears to depend on the temperature at which the action takes place, the oil produced in the first instance being again acted on by the excess of sodium present.

The liquid substance from the sodium action, which may be termed the "primary product," is in this case a yellow oil boiling in a vacuum of about 50 mm. at 335° , different preparations giving on analysis—

Substance 0.1751.

I. CO_2 0.5301 = C 80.21 per cent.

OH_2 0.1172 = H 7.43 "

Substance 0.1570.

II. CO_2 0.4757 = C 82.63 "

OH_2 0.0920 = H 6.51 "

Substance 0.1152.

III. CO_2 0.3492 = 82.67

OH_2 0.0761 = 7.33

Substance 0.0610.

IV. CO_2 0.1846 = 82.53

OH_2 0.0485 = 8.83

$\text{C}_{22}\text{H}_{20}\text{O}_2$ = C 83.5 H 6.3

To prove that the solid substance is a product of the action of sodium on the oils first formed, I have heated both the oil from ethylic phenylacetate boiling at 250° under 60 mm., and the one just described from propylic phenyl-acetate, with slight excess of sodium, and have obtained the same substance. Hydrogen was given off during the reaction.

The solid was obtained from the oil from ethylic phenyl-acetate, melting at the first crystallisation at 169° , and giving—

Substance 0.0606.

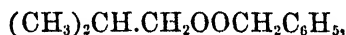
OH_2 0.0292 = C 79.79

CO_2 0.1773 = H 5.35

This solid body when warmed with acetic anhydride and a little zinc chloride (*Franchimont, Ber.*, 12, 2059), forms an acetyl compound melting at 100° after crystallisation from alcohol-ether.

The combustions of this substance are not very satisfactory, owing to the small quantity of material at my command, but they seem to indicate a monacetyl-compound.

These reactions so far have been extended to primary isobutylic phenyl-acetate—



a pleasant smelling limpid liquid, boiling at 147° (corr.), which gives isobutylic acetate, boiling at 113° , and an oil having about the same percentage of carbon and hydrogen as those obtained from the ethyl and propyl ethers, and to ethylic β -phenylpropionate, ethylic β -phenyl-acrylate, and benzylic phenyl-acetate. The latter is easily made by digesting benzylic chloride for a week with alcoholic potassic phenyl-acetate. It is a colourless liquid of faint odour, distilling unchanged at something over 300° . It boils constantly at 270° in a vacuum of 160 mm. Sp. gr. at 17° = 1.0938 (*Radzizewsky, Ber.*, 7, 1055).

On combustion the figures were obtained—

I.	II.	III.
80.50	C 79.54	C 79.67
6.70	H 6.25	H 6.24

Theory for $\text{C}_6\text{H}_5\text{CH}_2\text{COOCH}_2\text{C}_6\text{H}_5$ = C 79.65
H 6.19

Hydrogen is evolved by the action of sodium on this ether, and liquid products come over at about 100° .

On washing with water after the termination of the reaction, an oil is separated, and an aqueous solution obtained, from which SO_2HO_2 precipitates a liquid acid. From this, by boiling with a small quantity of water, phenylacetic acid may be separated, leaving another acid which is very slightly soluble, and separates from its solution in a

XXXV.—CONTRIBUTIONS FROM THE LABORATORY OF
THE ROYAL COLLEGE OF CHEMISTRY.

On the Action of Sodium on Phenyllic Acetate.

By W. H. PERKIN, Jun., and W. R. HODGKINSON.

IN previous communications to this Society and to the *Annalen*, the results of the action of metallic sodium on ethereal salts containing mixed fatty aromatic groups has been shortly described by one of us, and the results obtained led us to extend the inquiry to ethereal salts containing an aromatic, so-called, group of a simpler constitution than in those therein described.

We therefore commenced with phenyllic acetate, $C_6H_5OOCCH_3$, which was obtained by treating perfectly dry phenol with acetylic chloride in slight excess until hydrochloric acid gas ceased to be evolved. On distillation, a beautiful limpid liquid, boiling at 193° , and having a refractive power almost exactly that of crown glass, is obtained. A combustion gave—

Substance 0.1801.

$$CO_2 \ 0.4647 = C \ 70.37$$

$$OH_2 \ 0.0958 = H \ 5.90$$

$$\text{Theory for } C_8H_5O_2 = C \ 70.59$$

$$H \ 5.89$$

On warming this ether with sodium to about 100° , most violent action takes place, the temperature rising rapidly to above the boiling point of the acetate, and in some cases causing projection of the contents of the flask in which the operation is performed.

Hydrogen is evolved during the action, and considerable quantities of a light boiling liquid was carried over as vapour, and condensed in a receiver connected with the flask in which the action took place. This liquid had a most powerful odour of ethylic acetate, and on being fractioned distilled almost entirely at 76° , and gave on combustion—

$$0.1534 \text{ substance gave } CO_2 \ 0.3080 \text{ and } OH_2 \ 0.1244 = C \ 54.76$$

$$H \ 9.01$$

$$\text{Theory for acetic ether } (CH_3COOC_2H_5) = C \ 54.54$$

$$H \ 9.09$$

A portion was saponified with OKH, the potassic salt distilled with $SO_2(HO)_2$, and the distillate digested with argentic carbonate. The crystalline silver salt thereby obtained gave—

$$0.1030 \text{ gave } 0.0665 \text{ Ag} = 64.56$$

$$\text{Theory for } (CH_3COOAg) = 64.66$$

There is therefore no doubt that the liquid distilling over during the reaction is acetic ether.

The solid body remaining in the flask after the sodium has disappeared dissolves partially when treated with water, forming a dark coloured solution, and leaving a small quantity of a thick oil.

The watery solution, after shaking with ether to remove a little of the above oil, gives on acidifying with $\text{SO}_2(\text{HO})_2$ a copious precipitate of an oil, which was shaken with dilute ammonia, in which a great part remained insoluble.

This, separated from the ammoniacal solution, on fractioning distilled entirely between $180-190^\circ$, and solidified on cooling, forming needles characteristic of phenol, of which it gave all the reactions.

On acidifying the ammoniacal solution, after boiling with animal charcoal, a solid acid was precipitated, which on repeated crystallisation from hot water was obtained in white needles melting at 155° . An analysis gave—

$$\begin{array}{l} 0.2088 \text{ substance gave } \text{CO}_2 \text{ } 0.4645 \text{ and } \text{OH}_2 \text{ } 0.0858 = \text{C } 60.67 \\ \text{H } 4.56 \end{array}$$

$$\text{Theory for } \text{C}_6\text{H}_4 \begin{array}{l} \text{OH} \\ \text{COOH} \end{array} = \begin{array}{l} \text{C } 60.86 \\ \text{H } 4.34 \end{array}$$

which was further confirmed by the ferric chloride reactions, &c.

The aqueous solution, from which the phenol was precipitated by addition of sulphuric acid, was distilled with steam, and the acid distillate neutralised with baric carbonate, and the resulting barium salt converted into silver salt. An analysis of this gave the following:—

$$1.1105 \text{ substance gave } \text{Ag } 0.7159 = 64.47 \text{ per cent.}$$

$$\text{Theory for } \text{CH}_3\text{COOAg} = 64.66 \quad ,,$$

So far the products of the sodium action appear to be acetic ether, acetic acid, phenol, salicylic acid, and a thick oil. On submitting this to distillation, undecomposed acetate of phenyl first came off, then the thermometer rapidly rose to 300° . The remainder after distillation in a vacuum solidified on being subjected to a freezing mixture.

The crystalline mass was pressed between paper and crystallised from petroleum. As two distinct forms of crystals were observed to separate out on cooling; these were separated by repeated crystallisation from alcohol, in which one of them is almost insoluble.

The substance most soluble in alcohol, which may provisionally be called α , forms glistening white needles melting at 48° . When an alcoholic solution of this substance is warmed with potash, it produces a beautiful red coloration, destroyed by water, but reappearing on

evaporation. The specific gravity of this body is 1.026. On analysis it yielded the following figures:—

I.	II.	Theory for $C_{15}H_{12}O_3$.
C 75.13	74.55	75.00
H 5.30	5.4	5.00

The other substance, β , is much less soluble in alcohol, and crystallises in fine yellow needles melting at 138° . When warmed with alcoholic potash it forms a fine yellow crystalline compound. Its specific gravity is 1.076. On analysis it yielded the following figures:—

I.	II.	Theory for $C_{18}H_{14}O_4$.
C 73.2	73.54	73.4
H 4.6	4.63	4.7

From the proportions of ether and sodium employed in the reaction—



it is difficult to account for all the products by an equation.

The reaction may, however, consist first in the formation of sodium phenol, and acetic anhydride. Part of the latter reunites with the sodium phenol, and forms phenyl acetate and sodic acetate, and part is immediately reduced by the nascent hydrogen from the phenol sodium undergoing at the high temperature the decomposition shown to take place by Barth and Schreder (*Ber.*, 12, 417) by fusing phenol with sodic hydrate, when diphenol, phloroglucin, &c., are produced.

The two crystalline substances, α and β , may possibly be formed from an aceto-acetic ether compound, produced in the first instance and acted upon by sodium and sodium phenol, which, however, we must reserve for experimental proof.

In order to determine whether this was a general reaction, experiments were tried with cresyl acetate, prepared by treating cresol from Kahlbaum) with acetyl chloride. Cresyl acetate is a beautiful colourless liquid, boiling at 214° . An analysis gave—

	Theory.
C 72.26	72.00
H 6.65	6.66

This was treated with Na in the same manner as the phenyl acetate, and the low boiling liquid formed distilled off. This was evidently acetic ether. It was saponified, and the acid turned into Ag salt. On analysis the following numbers were obtained:—

0.1366 substance gave 0.881 Ag = 64.49 per cent.

Theory for CH_3COOAg = 64.66 „

Salicylic acid was also obtained, as in the action of Na on phenyl acetate, not methyl salicylic acid, as might have been supposed. It is therefore probable that acetic ether and salicylic acid are constant products of the action of Na on acetyl phenols.

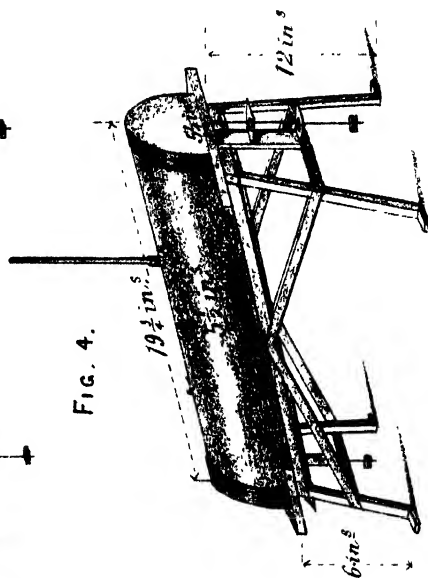
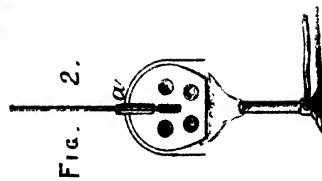
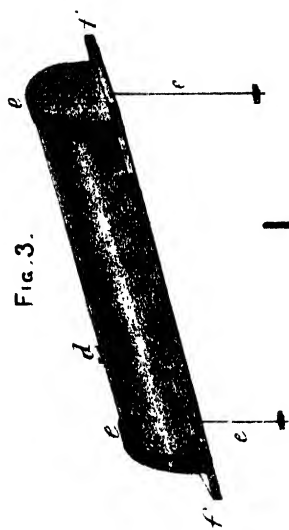
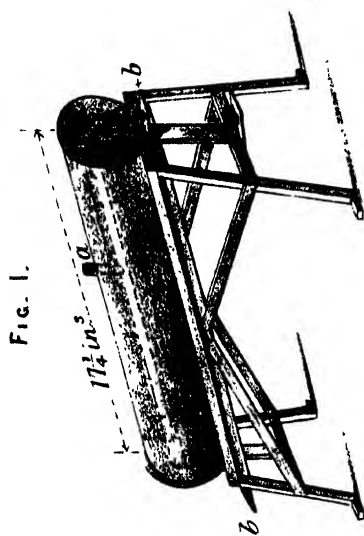
XXXVI.—*Note on an Improved Form of Oven for Heating Sealed Tubes, and avoiding Risks of Explosions.*

By WATSON SMITH, F.C.S., F.I.C., Assistant Lecturer and Demonstrator in Chemistry in the Owens College.

ANY one working much with sealed tubes, especially when high temperatures and resistance to great pressure are indispensable, may have observed that the usual forms of ovens in use generally possess some fault or drawback. For example, some are exceedingly safe in case of explosion, and the security of the thermometer is insured, but no temperature above 280° C. can be attained by them except by means of an extraordinary expenditure of heat and gas, and to reach even that temperature, three, four, or even in some cases, five gas burners may be required. Then, again, a considerable time is frequently required before the desired temperature is attained, and yet it may be incurring risk to leave the oven and trust to chance in coming back and finding the temperature almost reached. Yet again, ovens frequently require a long time to cool down, so that the tubes may be removed safely; and it may be required, as in perchlorinations or perbrominations, to open the tube, allowing exit to gas under pressure, to re-seal and then heat again. Much time may thus be either gained or lost, according to the efficiency or inefficiency of the form of oven employed.

It would thus appear that the best form of oven should (1) be capable of being *rapidly* heated up to *any* desired temperature, of course within reasonable limit. (2) It should be safe, both as regards the person and the thermometer. (3) It should be as simple as possible in construction, so as to render quick manipulation possible. (4) It should require as little expenditure of gas as possible, which means, heat should be economised as much as possible by it. (5) Finally, it should be capable of cooling down in as short a time as might be required, and this condition should be under a certain amount of control. I have recently had a form of oven constructed to fulfil all these requirements, which it does very satisfactorily. With one moderately large sized Bunsen burner, a temperature of about 420° to 440° C. can be obtained, and that in the course of a few minutes.

The following is a description of the oven:—Fig. 1 represents the internal body or tube-case of the oven, which would have been cylindri-



cal had it not been flattened below, as is best seen in the section, Fig. 2. It is made of strong sheet iron, the walls of the tubes being composed of stronger and thicker metal. The plate at the closed end of the oven is also of strong metal. There is a rim projecting about one-eighth of an inch above the body of the case, at either end, so that a space is left between the latter and its cover, Fig. 3, when the cover is adjusted upon it. At (*a*) is a tube passing an inch or two vertically downwards amongst the other tubes lying parallel. This tube exactly faces one in the cover, and in it is fitted a piece of glass combustion tube with a perforated cork, through which the thermometer is inserted. The piece of glass tube projects through the hole in the cover, so that the thermometer may be adjusted after the cover is in its place. As is seen in Fig. 1, the oven is inclined by standing in an iron frame with the hinder legs shorter than the fore legs. *bb* are pieces of iron with holes to admit the rods *cc* of the cover, which act as guiders. If the ends of these guiding-rods be furnished with a screw-thread, and a nut be fixed on each after adjusting the cover, the security of the thermometer in case of an extraordinarily violent explosion is perfectly secured. *ff* are handles by which the cover is lifted. *ee* are thick pieces of lead to weight the lid, and offer resistance in case of explosions; they form the ends of the cover. Fig. 4 shows the oven with lid and thermometer adjusted. At *d*, Fig. 3, in the cover, is a hole with cover or lid working on a hinge or screw, by which the hole can be wholly or partially closed. At the close of a heating up, if this hole be opened wide, after extinguishing the lamp, the oven is rapidly cooled by the current of air circulating around the space between the cover and tube-case, and passing out at the hole *d*.

All the apparatus here referred to, with the exception of the glass portion of it, may be had from Mr. Edmund Hargreaves, Higher Ormond Street, near Owens College.

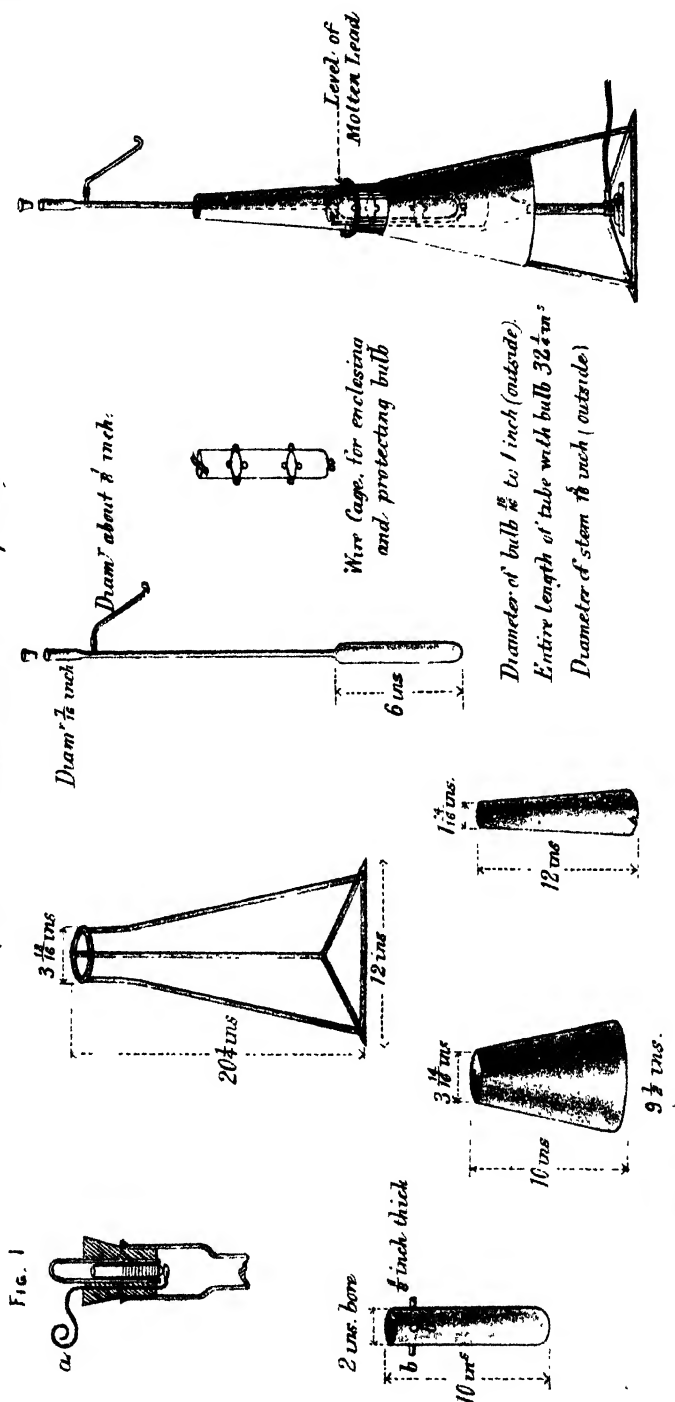
XXXVII.—*Note on a convenient form of Lead-bath for Victor Meyer's Apparatus for Determining the Vapour-densities of High Boiling Substances, together with a few Slight Modifications.*

By WATSON SMITH, F.C.S., F.I.C., Assistant Lecturer and Demonstrator in Chemistry in the Owens College.

HAVING had occasion at different times to determine by means of this excellent and simple method, the vapour-densities of several extremely high-boiling substances, I have had ample opportunities of observing

where any little improvements might with advantage be introduced. In the first place several advantages arise from cutting off the capillary gas-delivery tube at about half an inch from the main stem. This delivery tube or arm, to be connected to the main stem by a piece of caoutchouc tubing only when everything is adjusted for a determination. One advantage is that the fragility of the glass tube apparatus is considerably reduced. Another is, that the upper funnel of the lead-bath, to be described, will then pass readily over the stem. The delicacy, certainty, and accuracy of the process at the higher temperatures of the lead-bath may be ensured by (1) securing an even temperature, *i.e.*, a steady lamp flame under the bath. (2) Securing the stem of the apparatus as far as possible from currents of air of various temperatures. (3) Providing as far as possible against the danger of cracking the bulb, on introducing it into the bath. To attain these objects the following form of bath was ordered for construction, and adopted:—The apparatus of the bath consisted of four pieces. (A) The lead-bath itself, consisting of a piece of iron piping 9 or 10 inches long, $2\frac{1}{4}$ inches external, and 2 inches diameter. It is closed at one end, and rests supported in its iron tripod by four short projecting pieces, three of which are seen, *bbb*. The large funnel, acting as a flame-protector, C, is then placed over and around the whole, and allowed to slip into its place, where it adjusts itself around the limbs of the tripod, allowing a convenient space underneath for the introduction of the large Bunsen gas burner. The bulbous-glass apparatus, surrounded by its iron-wire cage, and well covered with soot by smoking in the luminous flame of a gas burner (see *Journ. Chem. Soc.*, June, 1880, p. 416), is now fixed at its clamp and brought so that the bulb dips just inside the mouth of the lead-bath, and stands an inch or a little less above the surface of the molten lead. Here it remains some minutes, when it is dipped a little lower, and at length is just brought in contact with the lead. The upper funnel (D) can now be easily brought over and around the glass tube of the vapour-density apparatus as it supports itself, floating on the lead. By protecting the stem through a considerable proportion of its length from currents of air of different temperatures, it plays a very important part, for without it, it is often necessary to wait some time till the little thread of water in the capillary tube has become steady. In course of the determination the results might be slightly affected too by the action on the stem of such currents. Before the bath is used the height at which the molten lead should stand before introducing the glass apparatus, is approximately ascertained by pouring water into the iron tube, and making a few trials with the bulb-tube. In the present case the iron bath was just half full of molten lead before introducing the bulb, so that it became just immersed.

Fig. 1 (a). Lothar Meyer's arrangement for letting fall the little tube with substance, without removing the stopper.
(Ber Deut Chem. Ges. XIII. N^o 9. p. 991).



If Lothar Meyer's recent improvement be adopted for letting fall the little tube with substance without removing the stopper (see Fig. 1 above) an increased precision and accuracy of manipulation will be then rendered possible. The apparatus should then be perfection.

(a), Fig. 1, is an iron wire bent as figured. Its undercoil supports the little tube, and at the right moment, a slight turn of the handle (a) will remove the support, and the tube will fall, without any displacement of air in the apparatus being necessary in moving or adjusting the stopper, as formerly.

XXXVIII.—*On the Mode of Application of Pettenkofer's Process for the Determination of Carbonic Acid in Expired Air.*

By WILLIAM MARCET, M.D., F.R.S., F.C.S.

SINCE the year 1875, my attention has been directed in the summer time to the influence of altitude on the phenomena of respiration, and results obtained have been published in an abstract form in the *Proceedings of the Royal Society for 1878 and 1879* (see also this Journal, 38, 483).

The first of these papers contains an account of the process I have adopted for the determination of the carbonic acid in expired air; a process which, although yielding trustworthy results after the introduction of a certain correction, was open to improvement. I have now succeeded in perfecting the mode of analysis, which in its present form yields correct and trustworthy results without any correction; while at the same time the apparatus required for that purpose is of a portable description.

The principle of the process is that of Pettenkofer's, the analysis being made by effecting the combination of the CO_2 in a known bulk of air with a solution of barium hydrate of known strength, and ascertaining afterwards volumetrically the amount of barium left in solution by means of oxalic acid.

After experimenting with vessels of various forms, in which the combination of the carbonic acid with barium hydrate might be effected, the simplest in shape was adopted—a hollow glass cylinder, or wide tube, holding about 1,500 c.c. and closed at both ends by india-rubber corks. This cylinder fulfilled a double object, first that of measuring out a certain bulk of the air to be submitted to analysis, and secondly that of enabling the air to be treated with the

normal solution of barium. A sketch of the apparatus I used is figured in my first paper (*Proceedings Royal Society*, 1878).

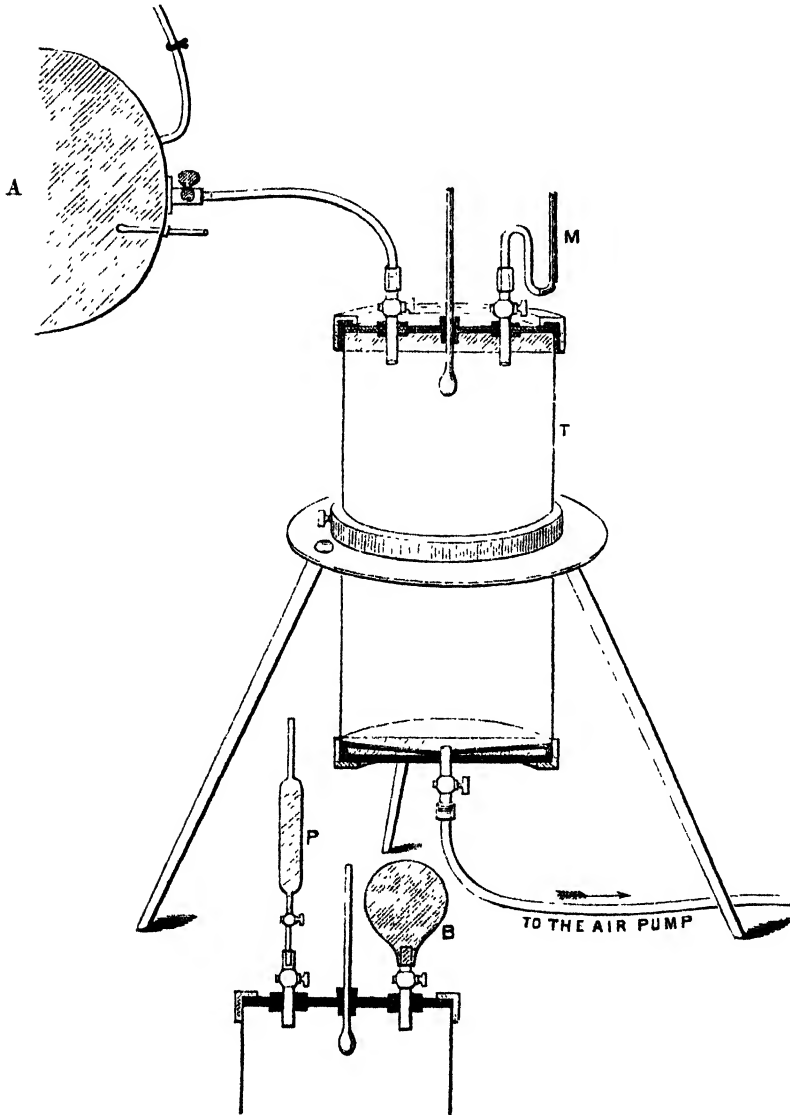
The air was collected from the lungs into a strong india-rubber bag of a capacity measured under a certain pressure, determined by a water-gauge, and which capacity varied, one bag holding 39.3 and another 68.4 litres under a pressure of 1 inch of water. The cylinder was filled with air from the bag, being fixed in the upright position to a light tripod, similar to those employed by photographers. In the experiments already published, the air was drawn into the tube by means of water; a solution of common salt, in order to lose no carbonic acid by absorption, had served the purpose instead of water in the first instance, but on trying water, and then testing it, I found it absorbed no carbonic acid. An objection to this method arose from the circumstance that the tube invariably retained a certain quantity of water, which adhered to the inside of the glass, and became mixed with the 100 c.c. of the alkaline solution used for the analysis. The results obtained might fairly, it is true, bear a mutual comparison, as the volume of water retained in the tube was nearly the same in every case, as ascertained experimentally, but they were really all too high; a correction therefore became necessary, which was calculated by determining the mean volume of water retained in the tube, and then taking into account the dilution of the normal solution arising from the admixture of this water with it. The correction was applied to all the determinations reported in my second paper, relating to work done on the Island and Peak of Teneriffe, while the estimations of CO_2 made previously were also corrected and introduced into the second paper under the form of means, so that they might be compared with the mean results from the experiments made at Teneriffe.

This last summer the use of water with the object of aspirating the air from the bag into the cylinder has been entirely given up, and I have had the satisfaction of working with an apparatus which will be considered, I think, free from objections, the present arrangement being available, not only for the determination of carbonic acid in air expired, but also in various other cases.

The hollow cylinder or tube I now employ is made of very thick glass, ground at both ends and closed by two round discs or slabs also consisting of very thick glass ground on the side in contact with the tube. Brass pieces are fitted over the ends of the cylinder, made to adhere firmly to the glass and bearing a thread, allowing of a brass ring to be screwed down tightly over them. The brass rings are flattened out at the top so as to keep the glass discs firmly down on the ends of the cylinder; a small quantity of grease previously applied to the rim of the tube secures an air-tight joint. As will be presently explained, a vacuum is produced in this cylinder by means of a

common one-barrel air-pump, and by opening a stop-cock, air from the bag is let into the tube ; a repetition of this same operation ensures the perfect filling of the cylinder with air from the bag.

APPARATUS FOR THE ANALYSIS OF AIR EXPIRED.



- A. Bag holding the air to be analysed.
- M. Manometer.
- T. Tube in which the air is treated with the solution of barium.
- B. Vulcanized india-rubber bag.
- P. Pipette holding 100 c.c. of the solution of barium.

I shall now beg to enter into the details of the construction of the present apparatus. The glass disc, the ground surface of which is applied to the upper end of the cylinder, is perforated with three round holes, and that which closes the lower end with only one. A thermometer graduated on its stem, a brass tube with a stop-cock, and another tube also supplied with a stop-cock are fitted through these openings. The thermometer is introduced through a common india-rubber cork, but the other tubes are inserted, air-tight, through studs of vulcanite, so that they cannot possibly be drawn in by atmospheric pressure, while the vacuum is being made in the cylinder. A single-barrel air-pump worked with both hands, while held with the feet, is connected with a brass tube supplied with a stop-cock, fitted through an aperture in the lower glass slab. This tube is also introduced through a stud of vulcanite; but the portion of the stud inside the cylinder is widened out so as to fill up the whole diameter of the cylinder; it is, moreover, slightly funnel-shaped, thus collecting the fluid towards the centre of the bottom of the tube, and allowing it to run out readily through the centre aperture into a small bottle, for subsequent analysis.

The operation is conducted as follows:—The cylinder, well washed and wiped out dry, is placed on its tripod, and, after slightly greasing the rims, the glass slabs with their ground sides in contact with the ground rims of the tube are screwed down upon them above and below. Next, the bag full of the air to be analysed is connected with one of the brass tubes of the upper disc, while a mercury manometer is screwed down tight on the other. The elastic pipe of the air-pump is now screwed to the brass tube fitting through the lower glass slab. I now open the cock of the tube in connection with the air-pump, while the two others are closed, and extract the air from the cylinder to a pressure of 20 or 30 millimetres, and then the air is let into the cylinder from the bag; this is repeated, and the cylinder becomes perfectly filled with a bulk of air equal to its own capacity. The cylinder I have been using holds 1,993 cubic centimetres. It is important, of course, to take into account the temperature of the air in the bag and in the tube while they are freely in communication with each other. This is easily done, as a thermometer passes into the bag through a neck in which it is fitted air-tight, and another thermometer gives the temperature of the air in the cylinder: both readings are recorded when found to be steady. Hence the bulk of air in the cylinder is measured under exactly the same pressure as that in the bag, and the reduction for the difference of temperature between the air in the bag and tube, if there be any, is easy to calculate.

The stop-cocks are now all closed (that of the tube connected with the air-pump had of course been shut immediately after making the

vacuum), and the pump-pipe and manometer are screwed off. I stated in my communications to the Royal Society, that a small pear-shaped vulcanised india-rubber bag had been used as a diverticulum for the air displaced by the introduction of the normal alkaline solution into the cylinder; such a bag was also employed in the present case. It was emptied of its air by being rolled between the fingers, and then its mouth was fitted over the tube to which the manometer had been formerly screwed; on the other hand, a pipette containing 100 c.c. of the normal solution of barium was introduced into the tube originally in communication with the air-bag. The stem of the pipette is served over with thread and wax so as to make it fit air-tight in the tube, and has a glass stop-cock, checking at will the fall of the solution. The stop-cock of the pipette and of the tube into which it is inserted are now opened, together with that of the tube connected with the diverticulum, and the alkaline solution falls into the cylinder, displacing a certain volume of air which finds its way into the pear-shaped vulcanised india-rubber bag; on grasping the pipette with the hand, after closing its mouth, the heat of the hand drives out the very last drop of the solution, so that the 100 c.c. may be relied upon to fall into the cylinder; the glass cock of the cylinder is then instantly shut.

The brass stop-cocks are now both closed, the empty pipette is taken out of the brass tube, and the cylinder removed from the stand to be agitated gently in a position nearly horizontal. After a minute or so the air in the diverticulum is forced back into the tube by pressure with the fingers, and the cock is closed, preventing any return of air into the small bag. The agitation is resumed, and after a lapse of ten minutes, I have found experimentally that the combination may be considered as complete. It is well to avoid agitating the fluid in the tube too violently, as such a manipulation appears to interfere with the subsiding of the precipitate of baric carbonate, and creates a difficulty when it is required to decant a certain bulk of the clear fluid for analysis. Nothing is now left to be done but to open the cocks and draw off the milky liquid into a small bottle holding about 100 c.c., which is immediately corked; the cork is finally dipped into melted paraffin.

The determination of the barium left in the clear solution, after precipitation of the carbonate, is proceeded with afterwards, certain precautions being taken to be presently stated.

The advantages of the method are manifold.

1st. The whole apparatus is of a portable nature, consisting summarily of a hollow glass cylinder, with its screws, glass slabs, and brass tubes, a mercury manometer, the vulcanised india-rubber diverticulum, a thermometer, a graduated pipette, and the air-pump with

its pipe, plus a light tripod as a stand for the cylinder; it is well to have at hand a spare thermometer and manometer, and a few pipettes, in case of accident.

2nd. The method may be accepted as giving results quite trustworthy, the capacity of the cylinder, together with the correction for temperature, yielding the exact bulk of air to be analysed. The bag containing the air expired is held up by an assistant while the tube is being filled; a certain degree of pressure is thereby exerted from the weight of the bag on the air inside it, having a tendency to increase the amount of air in the cylinder with which the bag is connected. The influence of this slight pressure must be very trifling, and has been neglected; if the correction was required it could be easily made.

3rd. If any doubt be entertained as to the complete combination of the carbonic acid in the cylinder with the barium, it is easy to withdraw a small quantity of air and to test it without detriment to the analysis. This is done by letting air into the india-rubber diverticulum, the stop-cock of the tube with which the diverticulum is connected being opened and then shut; the pear-shaped bag is then withdrawn, care being taken not to let out any air from it, and the sample thus extracted is passed through a solution of baric hydrate; 20 or 30 c.c. of air may thus be removed when the combination is nearly completed, without damaging the analysis. In large cylinders, such as that I have been using, holding 1,993 c.c. of air, the amount of air that can be collected in this way is but small, perhaps too small for testing purposes, because of the diminished pressure inside the cylinder, owing to the large quantity of carbonic acid absorbed by the barium; but this objection would not apply to smaller vessels, such as a cylinder holding about 1,509 c.c. of air, which would be large enough for the analysis of expired air.

The final analysis of the solution of barium can be done at any time, say within a month, and even a longer period, as the cork, covered with paraffin, may be considered practically impervious to air; 25 c.c. of the clear solution, after the precipitate has subsided, are decanted and mixed with 100 c.c. of distilled water ascertained to be free from carbonic acid. The mixture is made in a cylindrical vessel holding but little more than 125 c.c., and which is closed with an india-rubber cork. The fluid is shaken and poured into a 50 c.c. burette, afterwards closed with a cork connected with a tube holding pieces of potassic hydrate, through which air passes into the burette as the fluid is drawn out of it. 5 c.c. of a solution of oxalic acid of such a strength that 1 c.c. = 1 mgrm. CO_2 , are measured out into a beaker, and two or three drops of a solution of turmeric added. The amount of fluid from the burette necessary to neutralise the acid is

then determined. I have found it necessary, in order to guard against error, to renew frequently the solution of oxalic acid; after a week or ten days, especially in warm weather, the strength of the solution can hardly be relied upon. I have frequently used simultaneously two solutions of oxalic acid made at different times; great accuracy can be obtained by adopting these various precautions. I prefer the present plan to the dropping of the oxalic acid solution from the burette into a measured volume of the alkaline solution, thus avoiding any error from the carbonic acid present in the atmosphere. As to the time required for the above manipulations, about 25 minutes to half an hour will be wanted, so far as the collection of the milky fluid in the bottle is concerned, and the remainder of the work can be done subsequently at the rate of two or three different analyses per hour.

I subjoin an illustration of the calculations of the analysis which offer no difficulty.

Calculations of the Analysis.

Volume of the bag full of expired air, 39.3 litres, under 1 inch pressure of water.

Time to fill the bag with expired air, 353 seconds.

Volume of cylinder, 1,993 c.c.

Temperature of air in bag, 60.0°.

Temperature of air in cylinder, 58.0°.

25 c.c. of the clear solution of barium decanted after precipitation and mixed with 100 c.c. of water.

1. 5 c.c. oxalic acid are neutralised by 17.50 c.c. of the mixture.

2. " " " 17.55 " "

3. " " " 17.60 " "

4. " " " 17.65 " "

Mean..... 17.57

In many, perhaps most analyses, the four determinations agree closer than in the present case.

$$125 : 25 = 17.57 : x.$$

$x = 3.514$ pure undiluted solution neutralise 5 c.c. oxalic acid.

$$3.514 : 0 : 305 \text{ CO}_2 = 100 : x.$$

$x = 0.1423 \text{ CO}_2$ corresponding to 100 c.c. of the clear solution of barium.

CO₂ corresponding to 100 c.c. normal alkaline solution . . . 0.2730

CO₂ corresponding to 100 c.c. alkaline solution after precipitation 0.1423

0.1307

Grams CO₂ in cylinder.

2 L 2

Correction of volume of air in cylinder for 2° F. = 15 c.c.

$$1993 + 15 = 2008.$$

$$(\text{Litres}) 2.008 : 0.1307 = 39.3 : x.$$

$$x = 2.588 \text{ gram CO}_2 \text{ in the bag.}$$

$$\begin{array}{cc} \text{Seconds.} & \text{Seconds.} \\ 353 : 2.558 & = 60 : x. \end{array}$$

$$353 : 2.558 = 60 : x.$$

$$x = 0.435 \text{ gram CO}_2 \text{ expired per minute.}$$

I have records of upwards of 353 determinations of carbonic acid in air expired under various circumstances, and hope to continue the inquiry.

XXXIX.—*Determination of Nitrogen in Carbon Compounds.*

By CHARLES E. GROVES.

THE methods employed for the determination of the amount of nitrogen in carbon compounds depend on two principles—the decomposition of the substance in presence either of a reducing or of an oxidising agent.

The well-known method originally devised by Will and Varrentrapp of heating the substance with soda-lime, whereby the nitrogen present in it is liberated as ammonia and estimated as such, and the various modifications of this process depend on the reducing action of carbon compounds rich in hydrogen, that is, in which the number of hydrogen atoms is greatly in excess of that of the oxygen atoms: it has the advantage that the combustions can be rapidly made and require but little attention, although the results obtained are usually somewhat low: this—from the recent careful examination of the process by Prehn and Hornberger (*Landw. Versuchs.-Stat.*, 24, 21)—would seem to be due chiefly to the air present in the tube, and may be obviated to a great extent by special manipulation.

The methods involving the use of oxidising agents are of two kinds—the one introduced by Dumas, in which the substance is completely oxidised and the amount of nitrogen evolved in the gaseous state is determined, and the numerous modifications of this process, including the extremely accurate one invented by Frankland and Armstrong; the other of special and restricted application, proposed by Wanklyn, Chapman, and Smith, where the substance is submitted to a limited oxidation with an alkaline solution of potassium permanganate, and the amount of ammonia produced is estimated. The

present communication is a brief account of certain modifications in the first mentioned of these oxidation processes—Dumas' method.

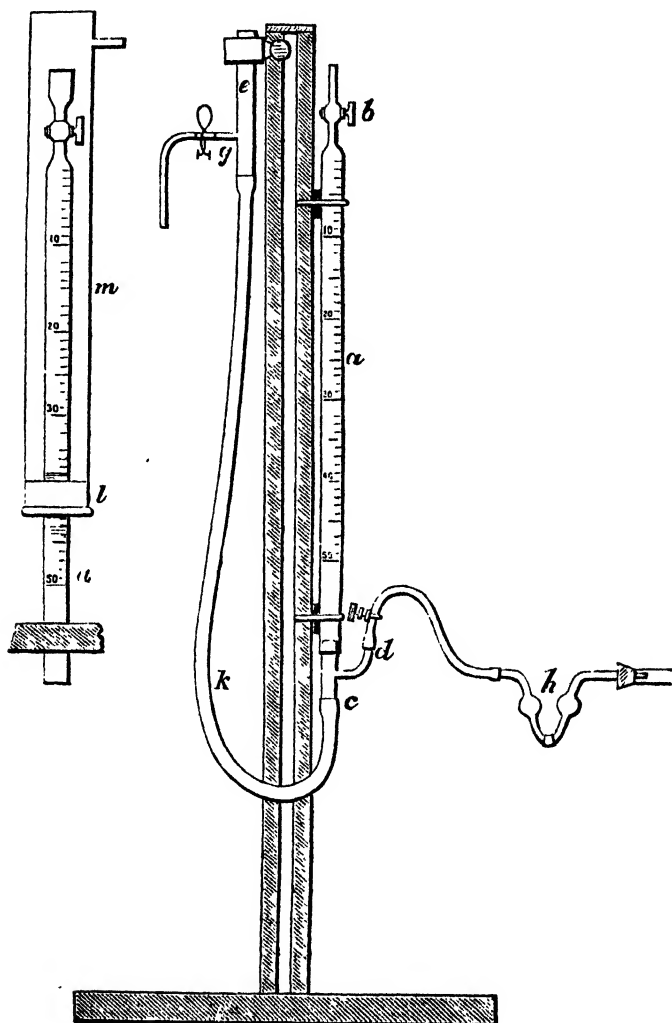
About a twelvemonth ago I had occasion to make several nitrogen determinations by burning the substance with copper oxide, and employed Zulkowsky's apparatus (*Annalen*, 182, 296) for collecting and measuring the nitrogen: this, in many respects, is a great improvement on the method originally used by Dumas, especially as no mercury is required. Its use, however, is attended with some inconvenience, which it seemed possible to obviate by using another form of apparatus. As the arrangement devised has been found to be simple and convenient, it may be advisable to publish some account of it, especially as Schwarz (*Ber.*, 13, 771; see also Ludwig, *ibid.*, 883, and Schiff, *ibid.*, 885) has recently described an improved form of Zulkowsky's apparatus which resembles it in one of the details.

The apparatus consists of a measuring tube, *a*, 18 inches long and 0.5 inch in *internal* diameter, graduated for 50 c.c.*, each division being equal to 0.1 c.c., and furnished with a well-made glass stop-cock, *b*, at the upper end: the best lubricant for this stop-cock is the soft paraffin, known as "vasilene," which is quite unaffected by strong potash solutions. A short tube, *c*, 3 inches long and 0.4 inch *external* diameter, is fitted into the lower end of this by means of a short piece of caoutchouc tubing which is slipped over the end of the tube, *c*, and is of such a size that when the tube *c* is inserted into the lower end of the measuring tube, the annular space between the two tubes is completely filled by the caoutchouc, thus forming an air-tight joint. A small tube, *d*, fused into the side of *c*, and bent upwards at right angles, serves to connect the apparatus with the combustion tube. The tube *c* is connected by means of a caoutchouc tube, *k*, about 27 inches long, with another glass tube, *e*, of precisely the same diameter as the measuring tube, and having a narrow piece of tube, *g*, 1 inch long, fused into the side; a piece of caoutchouc tube is attached to this, and is closed by a pinch-cock when not required for drawing off the excess of potash from the tube *e*. The whole is mounted on a convenient stand which allows of the tube *e* being raised or lowered with ease.

In making a nitrogen determination, the tube, *d*, is connected, as in Zulkowsky's arrangement, with a double bulb tube, *h* (containing a globule of mercury), by means of a caoutchouc tube: this is then clamped, the tube *e* is raised above the level of the stop-cock, *b*, which is left open, and the apparatus is filled with potash solution (1.25 sp. gr.), taking care that no air bubbles lodge in the caoutchouc tube, *k*. A

* For a measuring tube of 80 c.c. *a* should be 0.65 inch in *internal* diameter and 0.55 *external* diameter. The tubes *c* and *e* should be drawn out smaller at the lower ends, so as not to use too large a caoutchouc tube to connect them.

pipette capable of holding about 70 c.c. is inserted into the upper open end of *e*, through a perforation in a tightly-fitting cork, and the tube, *e*, and pipette are then lowered until the level of the potash



in *a* sinks below the side tube *d*, the clamp between *d* and *h* is then opened, and the "bicarbonate of soda," or mixture of sodium carbonate and potassium dichromate at the end of the combustion tube remote from *h*, is gently heated until the air is entirely expelled. Under ordinary circumstances this takes about 10 minutes, the bubbles passing through *h* at the rate of 100—120 per minute: the metallic copper at the anterior end is next heated to bright redness, which

takes 7 or 8 minutes more, and the tube, *e*, with the pipette is then gradually raised, the potash solution rising in the measuring tube and expelling the air. As soon as the level of the liquid reaches the stop-cock, this is closed, and the pipette may be removed from *e*.

If the carbonic anhydride has been passed sufficiently long so as to entirely expel the air from the combustion tube, each bubble as it rises in the measuring tube will be absorbed, becoming almost invisible by the time it reaches the top. If the bubbles of gas are not completely, or at all events almost entirely absorbed, the current of carbonic anhydride must be continued until they are, the stop-cock being opened for a moment to allow the small quantity of air to escape.

As soon as the air is entirely expelled, the tube *e* is lowered until the level of *g* is about 1 inch below that of *d*; the combustion is then proceeded with in the usual manner. A piece of glass tube bent at right angles is adapted to *g*, and the pinch-cock removed, so that the excess of potash solution as it is gradually expelled from the measuring tube during the combustion, may flow out into a small flask placed to receive it.

Instead of allowing the apparatus to stand for some hours in a room where the temperature is constant, before observing the volume of gas, the measurement may be made with greater accuracy, and within half an hour of the completion of the combustion, if the measuring tube be provided with a water jacket. For this purpose a stand, somewhat different from that represented in the figure, must be employed, the tube *a* being fixed and supported by its lower end only; a large vulcanised caoutchouc cork, *l*, slides easily over the measuring tube, and when the combustion is finished is placed at the level of the potash solution in *a*. This cork serves to close the bottom of the wide glass tube, *m*, forming the water jacket, which is now placed over the measuring tube, and through which a current of water can be passed. It is necessary to have the bottom of the water jacket at the same level as the potash solution in *a*, otherwise the liquid in the two limbs of the apparatus would be at different temperatures, and consequently of different densities.

Amongst the advantages attending the use of this apparatus, are its great simplicity, the comparatively small quantity of potash solution required, and the fact that the combustion being carried out under the ordinary atmospheric pressure, or under slightly diminished pressure, it is quite unnecessary to wrap the tube in wire gauze to prevent it "blowing out;" not the slightest tendency to do so is shown, even where the tube is most intensely heated, namely, at the anterior end containing the metallic copper. In this respect it is far superior to Zulkowsky's apparatus or the various modifications of it recently described. As the apparatus is made in several parts, without rigid

joints, there is little tendency to fracture, and if either of the two comparatively fragile parts, *c* or *e*, is broken, it is easily replaced.

As the modification of Liebig's method for the determination of carbon and hydrogen, which was originally introduced by Piria (*Annalen*, 195, 298), amongst its other advantages, allowed of the same combustion tube being used many times, it seemed probable that in the Dumas method, if a separate tube could be used to contain the substance employed to generate the carbonic anhydride, here also the same combustion tube might be used over and over again. This was found to be the case.

Into a tube of hard glass 23 inches long, and from 0.40 inch to 0.45 inch internal diameter, and having the ends fused and turned out, a plug is inserted at a distance of 6 inches from one end; this plug consists of a core of copper wire-gauze, about 0.8 inch long, surrounded with asbestos, and fits very tightly into the tube, so that it cannot be removed by any amount of shaking; under these conditions, if asbestos alone were used, there would not be a free passage for the gases, but the wire-gauze core obviates this difficulty. As much copper oxide is introduced into the tube as will occupy a length of about 9.5 inches, and a portion of this is then shaken out into a glass dish, leaving 4 inches in the tube; the copper oxide taken out is mixed in the glass dish with the substance to be analysed, returned to the tube, which is washed out with a little more copper oxide (the washings should occupy about 1.5 inch of the tube); lastly, a plug of copper wire-gauze is inserted to keep the oxide in its place. This plug is made by winding a strip of wire-gauze, about 1 inch wide, round a stout piece of copper wire twisted into a loop at one end, and bent at the other, so that the wire-gauze cannot slip off when a hook is inserted into the loop, and the plug is withdrawn after the combustion is finished.

The "bicarbonate of soda," or mixture of sodium carbonate and potassium dichromate, is contained in a tube about 7 inches long, of the same diameter as the combustion tube, closed at one end and turned out at the other. The carbonic anhydride mixture is kept in its place by a plug of asbestos, leaving about 1 inch of the tube clear. This apparatus for generating carbonic anhydride is connected with the combustion tube by means of a stout piece of quill tubing, some 4 or 5 inches long, whose external diameter is somewhat smaller (about 0.05 inch) than the internal diameter of the combustion tube, the joints being made by means of a short piece of caoutchouc tubing of the requisite size being slipped partly over the end of the smaller tube, which is then inserted into the larger one, so that the annular space between the inner and outer tubes is filled with caoutchouc, thus form-

ing a perfectly air-tight joint.* There should be a free space of about 3.5 inches between the wire gauze plug in the combustion tube and the caoutchouc joint, to prevent the latter being destroyed by the heat.

When the tube for generating the carbonic anhydride has been connected with the combustion tube, a coil of copper wire-gauze, which has been recently reduced, is inserted into the other end of the combustion tube, and the double bulb tube, *h*, is connected by means of an annular caoutchouc joint. This tube, *h*, must be supported, as otherwise its weight would cause distortion of the combustion tube as soon as the latter became strongly heated. When a passage for the gas has been made, the combustion is proceeded with in the usual way, the only precaution necessary being that as soon as the fore part of the tube containing the metallic copper and pure copper oxide is red hot, the wire-gauze plug, and about an inch of the oxide at the other end, should be heated, to prevent any of the unoxidised products from condensing at that end and escaping complete combustion.

I find that very accurate results may be obtained by this method, especially if the precaution be taken when the combustion of the substance is terminated, to expel the gas from the tube by passing carbonic anhydride for the same time, and as nearly as possible at the same rate as that which was required to expel the air from the tube before commencing the combustion.

To make another combustion in the same tube, it is allowed to cool, the carbonic anhydride apparatus is disconnected and recharged, the wire-gauze plug is drawn out of the combustion tube by means of a wire bent into a hook at one end, and the partly reduced copper oxide is removed; this is easily done after it has been stirred up with a wire flattened at one end. The tube is then ready for recharging. If the copper coil at the fore part of the tube requires to be again reduced, this may be done *in situ*, by heating it in a current of mixed CO_2 and CO , produced by warming oxalic acid with concentrated sulphuric acid; this is preferable to hydrogen.

By this method the same tube may be employed for from 6 to 12 combustions, if ordinary care be taken.

Some analyses made by this method to test its trustworthiness gave very satisfactory results. The substances chosen as representative were ammonium oxalate, an impure peptone, and a volatile nitro-derivative, dinitrobenzene. The last-mentioned was made from benzene which had been carefully purified by treatment with sulphuric acid and repeated crystallisation. Column 2 gives the weight of the substance taken in grams; Column 3, the nitrogen in cubic centimeters,

* This joint might be called the *annular caoutchouc* joint. In making it a trace of glycerol or vasiline should be used as a lubricant.

at 760 mm. and 0° C., corrected for aqueous vapour; Column 4, the corresponding weight of the nitrogen in grams.

Substance.	Weight taken.	c.c. N.	Grams N.	Found.	Theory.
(NH ₄) ₂ C ₂ O ₄	0·2370	42·816	0·053715	22·66	22·58
.....	0·1660	29·559	0·037084	*22·34	„
C ₆ H ₄ (NO ₂) ₂	0·2540	33·608	0·042164	16·60	16·67
„	0·2145	28·491	0·035744	16·66	„
Peptone	0·2660	24·329	0·030522	11·74	?
„	0·2200	20·543	0·025772	11·72	?

In order to reoxidise the partly reduced copper oxide, it is usually recommended that it should be moistened with nitric acid, and then strongly ignited; in this way, it is often necessary to moisten with water and re-ignite several times before an oxide is obtained which will not give off nitrogen when employed in the Dumas process, and it must always be looked on with suspicion until it has been tested by a blank combustion or otherwise. The spent oxide may, however, be readily and effectually oxidised by heating it in a current of air, in a very simple manner. An earthenware tube of small bore, such as the stem of a clay tobacco-pipe, is passed down to the bottom of the crucible containing the oxide, and a current of air is passed through it by means of an aspirator, whilst the crucible is heated to redness. In the course of an hour or so the reduced copper will be completely reoxidised.

XL.—On the Action of Air upon Peaty Water.

By Miss LUCY HALCROW and E. FRANKLAND, F.R.S.

In his paper on river water (*Chem. Soc. Jour.*, 1880, 295), Dr. Tidy contends that the peaty matter in running water is rapidly oxidised. He instances the water of the Shannon, which he alleges loses more than 38 per cent. of its organic elements by oxidation during a flow of only one mile, and the water supply of a town in the north of England, which, as appears from the analysis of two samples similarly loses 50 per cent. of its organic carbon during a flow of less than four miles through an open brickwork conduit.

* In this instance the precaution was not taken of passing the carbonic anhydride through the apparatus after the termination of the combustion for the same length of time as when expelling the air.

If peaty matter in solution in water possesses this extraordinary affinity for oxygen at ordinary temperatures, it cannot be necessary to appeal for proofs of it to large bodies of water, which are always more or less liable to alterations in the proportion of their organic elements, from other causes.

We have therefore studied, upon an experimental scale, the action of exceptionally strong peaty water upon atmospheric air, so as to ascertain how far air loses oxygen by contact with such water. For this purpose, we have submitted to eudiometrical analysis limited volumes of atmospheric air which had been exposed for periods of varying duration to the action of large volumes of peaty water from unpolluted mountain sources.

Before describing the results of these experiments, however, we will here interpolate two analyses of the same sample of unpolluted peaty water. The second was made after an interval of 70 days, the water having half filled a colourless glass bottle, 10 inches high, and $5\frac{3}{4}$ inches in diameter, closed only by a piece of thin filter paper, so as to exclude dust but secure a continued interchange between the internal and external air, if there should be any variation in the composition of the former. The bottle and its contents were freely exposed to the strongest daylight obtainable through a window about 12 feet square.

Results of Analysis expressed in parts per 100,000.

	Total solid matters.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Chlorine.	Hardness.	Remarks.
Composition of the peaty water used.	4.58	0.759	0.033	0	0	0.033	0.70	2.6	Yellow and turbid.
Ditto after exposure to air and light for 70 days.	4.26	0.718	0.026	0	0	0.026	0.70	2.7	Yellow and clear.

Thus after a free exposure of 70 days to air and light, in a stratum only 5 inches deep, this peaty water had suffered a loss of only 6 per cent. of its organic elements. We could not with certainty, however, attribute this loss to oxidation, because the water submitted to the first analysis was turbid, whilst that used for the second was clear, a slight brownish sediment having been deposited at the bottom of the bottle.

Effect upon Air of prolonged Exposure to Peaty Water in Daylight, but without Agitation.

These experiments were made upon air which had been in contact with comparatively large volumes of unpolluted mountain water (containing between 0·4 and 0·5 part of organic elements per 100,000), in accurately stoppered bottles for more than a year. The small quantity of air required for analysis was expelled by the injection of distilled water to the bottom of the bottles. The gases were collected, and their analyses performed over mercury.

I. Analysis of air which had been standing in contact with upland surface water from March 24th, 1879, to May 3rd, 1880:—

	Pressure.	Temperature.
Original gas (dry)	204·5 mm.	17·7°
After absorption of CO ₂ (dry).	204·3 „	„
After admission of H (dry)	439·9 „	„
After explosion (dry)	312·4 „	„

These numbers correspond to the following percentages by volume:—

CO ₂	0·10
O	20·78
N	79·12
	<hr/>
	100·00

The water, after admixture with the distilled water used to expel the air, still contained 0·354 part of organic carbon, and 0·069 of organic nitrogen in 100,000 parts. Originally the unmixed water contained 0·399 part of organic carbon, and 0·074 of organic nitrogen in 100,000 parts. It is the only one of the four samples used in this series of experiments, of which an initial analysis was made.

II. Analysis of air which had been in contact with upland surface water, from March 25th, 1879, to May 5th, 1880. The contents of this bottle were well shaken up several times during the 48 hours immediately preceding the examination of the air.

	Pressure.	Temperature.
Original gas (dry)	460·8 mm.	17·5°
After absorption of CO ₂ (dry)	460·1 „	„
Ditto new measurement for combustion (dry)	183·9 „	„
After admission of H (dry)	342·2 „	„
After explosion (dry)	227·2 „	„

The following percentages by volume are calculated from these readings:—

CO ₂	0·15
O	20·81
N	79·04
	<hr/>
	100·00

The water, after the addition of the distilled water, still contained 0·354 part of organic carbon, and 0·09 part of organic nitrogen in 100.000 parts.

III. Analysis of air which had been standing in contact with upland surface water, from March 26th, 1879, to May 7th, 1880. This bottle was nearly full of water, and consequently contained but very little air.

	Pressure.	Temperature.
Original gas (dry)	417·4 mm.	20·0°
After absorption of CO ₂ (dry).	416·6 „	„
Ditto new measurement for combustion (dry)	300·9 „	20·4°
After admission of H (dry) ..	509·0 „	„
After explosion (dry)	320·6 „	„

These numbers correspond to the following percentage volumes:—

CO ₂	0·19
O	20·83
N	78·98
	<hr/>
	100·00

After admixture of distilled water as before, the water contained 0·471 part of organic carbon and 0·075 part of organic nitrogen in 100,000 parts.

IV. Analysis of air which had been standing in contact with unpolluted mountain water, from April 17th, 1879, to April 30th, 1880:—

	Pressure.	Temperature.
Original gas (dry)	536·0 mm.	18·1°
After absorption of CO ₂ (dry).	535·2 „	„
Ditto, new measurement for combustion (dry)	219·5 „	„
After admission of H (dry) ..	357·6 „	„
After explosion (dry)	221·1 „	„

From these numbers the following percentage volumes are calculated:—

CO ₂	0.15
O	20.69
N	79.16
	<hr/>
	100.00

100,000 parts of the mixture of original water and distilled water left in the bottle still contained 0.408 part of organic carbon, and 0.070 part of organic nitrogen.

All these results prove that the extent to which the peaty matter of the upland water was oxidised, in periods of more than a year, was very small indeed; for the carbon alone of the peaty matter in each bottle was more than sufficient to take up the whole of the oxygen from at least 100 c.c. of air, whilst, as the analyses show, not more than $\frac{1}{160}$ at the maximum, was removed from less than 1 litre of air.

Effect upon Air of Violent Agitation with Peaty Water.

For these experiments, bottles of about 500 c.c. capacity, with accurately fitting stoppers, were half filled with very strong peaty water, collected from a mountain bog, and containing in 100,000 parts, 2.912 parts of organic carbon and 0.168 part of organic nitrogen, but no ammonia and no nitric nitrogen. The stoppers were greased with resin cerate and carefully secured, and the bottles were kept in an inverted position throughout the whole course of the experiments. At the conclusion of each experiment, the air was expelled by distilled water, as before, and collected over mercury. Immediately before use 100 volumes of this peaty water contained, according to Mr. Frank Hatton's analysis, 2.01 volumes of air in solution, possessing the following percentage composition:—

CO ₂	1.99
O	31.96
N	66.05
	<hr/>
	100.00

V. Analysis of air which had stood over an equal volume of peaty water for 19 hours in darkness, with frequent agitation. Temperature about 18°. The water remained clear and unchanged in colour.

	Pressure.	Temperature.
Original gas (dry)	469.6 mm.	16.1°
After action of KHO (dry) ..	468.5 "	"
Ditto remeasured for combustion (dry)	354.8 "	21.4
After admission of H (dry) ..	595.7 "	"
After explosion (dry)	374.1 "	"

From these readings the following percentage volumes result :—

CO ₂	0.23
O	20.77
N	79.00
	<hr/>
	100.00

VI. Analysis of air which had been frequently shaken up with an equal volume of peaty water for 64 hours, viz., 30 hours in darkness, 28 hours in daylight, and 6 hours in sunlight. Temperature about 18°. The water remained clear and unchanged in colour.

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	424.0 mm.	20.0°	340.2 mm.	21.6°
After absorption of CO ₂ (dry)	422.9 "	"	339.5 "	"
Ditto remeasured for combustion (dry) ..	301.8 "	"	241.5 "	"
After admission of H (dry)	459.1 "	"	382.2 "	"
After explosion (dry) ..	270.5 "	"	231.2 "	"

These numbers denote the following percentage volumes :—

	I.	II.	Mean.
CO ₂	0.26	0.20	0.23
O	20.78	20.80	20.79
N	78.96	79.00	78.98
	<hr/>	<hr/>	<hr/>
	100.00	100.00	100.00

VII. In this experiment the bottle containing equal volumes of air and peaty water was securely tied to a wooden cradle, which was fastened to the connecting rod of a horizontal steam engine making 100 strokes per minute. Thus, in $10\frac{1}{2}$ hours, the contents of the bottle received 126,000 violent concussions. The engine was in a well lighted workshop, and for more than 9 out of the $10\frac{1}{2}$ hours the shaking took place in daylight. Altogether the contents of the bottle were 48 hours in darkness, $75\frac{1}{2}$ hours in daylight, and $8\frac{1}{2}$ hours in sunlight. The water was scarcely changed in colour, but it was slightly turbid when it came off the engine, and a very small quantity of dark brown sediment was rapidly deposited. The temperature near the engine was about 26° C., but during the rest of the time, it varied from 17° to 20°. An analysis of the enclosed air at the end of the experiment, gave the following results :—

	Pressure.	Temperature.
Original gas (dry)	405·0 mm.	17·3°
After absorption of CO ₂ (dry).	404·5 "	"
Ditto remeasured for combustion (dry)	289·0 "	"
After admission of H (dry) ..	478·9 "	"
After explosion (dry)	298·8 "	"

These readings correspond to the following percentage volumes :—

CO ₂	0·12
O	20·75
N	79·13
	<hr/> 100·00

VIII. The next experiment was made with the view of testing the effect of an increase of temperature. The bottle and its contents were kept during the day as nearly as possible at a temperature of 30°, by being immersed in warm water contained in a clear glass vessel. During the night, however, the temperature fell to 16° or 17°. Altogether the contents of this bottle were 64 hours in darkness, 112 hours in daylight, and 16 hours in sunshine. The water at last was slightly turbid, and deposited a small quantity of a brownish sediment, but its peaty tint was not perceptibly affected. At the end of these periods a sample of air was withdrawn and submitted to analysis with the following results :—

	Pressure.	Temperature.
Original gas (dry)	395·5 mm.	21·9°
After absorption of CO ₂ (dry).	394·7 "	"
Ditto new measurement for combustion (dry)	279·8 "	20·1
After admission of H (dry) ..	438·8 "	"
After explosion (dry)	263·9 "	"

These numbers lead to the following percentage volumes :—

CO ₂	0·20
O	20·79
N	79·01
	<hr/> 100·00

Effect upon Air of Violent Agitation with Waters free from Oxidisable Organic Matter.

For the sake of comparison we have extended these experiments to the deep well waters of the Kent and Colne Valley Companies, and to

organically pure distilled water. The small quantity of organic matter which these deep well waters contain having survived the oxidising effect of percolation through vast thicknesses of chalk, may be regarded as unattackable at ordinary temperatures by free oxygen. The Kent Company's water contains a large proportion of bicarbonate of lime, the hardness of this sample being no less than 26° , of which a large portion is temporary. The Colne Valley Company's water, on the other hand, having been softened by Clark's process, retained a hardness of only $3\cdot7^{\circ}$, and was presumably deprived of carbonic acid both free and combined. The organically pure distilled water was allowed to aërate itself by being put into a large beaker, covered with filter-paper to exclude dust.

The Kent and Colne Valley Company's waters actually used contained in 100,000 parts the following quantities of organic elements:—

	Kent.	Colne Valley.
Organic carbon.....	0·093	0·066
„ nitrogen.....	0·011	0·015

IX. Analysis of air which had been in contact with the Kent Company's water for 44 hours, the bottle having been in darkness for 16 hours, in bright diffused daylight for 22 hours, and in sunshine for 6 hours. The water remained bright and clear:—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	296·8 mm.	20·0°	484·5 mm.	16·3°
After absorption of CO ₂ (dry)	296·1 „	„	483·2 „	„
Ditto, new measurement for combustion (dry)	296·6 „	„	290·7 „	„
After admission of H (dry)	462·6 „	„	446·6 „	„
After explosion (dry).	277·1 „	„	264·5 „	„

These readings correspond to the following percentage volumes:—

	I.	II.	Mean.
CO ₂	0·23	0·27	0·25
O	20·80	20·82	20·81
N	78·97	78·91	78·94
	100·00	100·00	100·00

X. Analysis of air which had been in contact with the Colne Valley Company's water for 63 hours, the bottle having been 24 hours in darkness, 35 in bright daylight, and 4 in sunlight:—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	386·8 mm.	18·6°	—	—
After absorption of CO ₂ (dry).....	386·8 „	„	—	—
Ditto, new measure- ment for combus- tion (dry)	257·2 „	17·0	278·0 mm.	20·6°
After admission of H (dry).....	422·7 „	„	429·9 „	„
After explosion(dry).	260·9 „	„	255·0 „	„

These numbers express the following percentage volumes:—

	I.	II.	Mean.
CO ₂	0·00	—	—
O	20·97	20·97	20·97
N	79·03	79·03	79·03
	100·00	100·00	100·00

Like most deep well waters, the Colne Valley Company's probably arrives at the surface with mere traces of oxygen in solution; but if so, it had acquired its full complement of atmospheric oxygen before it was used for this experiment, since it scarcely withdrew an appreciable amount from the air with which it was shaken up. By undergoing Clark's softening process, however, this water is deprived of every trace of carbonic anhydride, and it can only, of course, reabsorb its full amount of this from the air with extreme slowness. Hence the air shaken up with this water was entirely deprived of its carbonic anhydride.

XI. Analysis of air which had been in contact with organically pure distilled water for 72 hours; the bottle was in darkness for 24 hours, in daylight 42 hours, and in sunlight 6 hours:—

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	479·0 mm.	19°	360·3 mm.	18·3°
After absorption of CO ₂ (dry).....	478·6 „	„	359·9 „	„
Ditto, new measure- ment for combus- tion (dry)	342·0 „	19·8°	214·7 „	„
After admission of H (dry).....	504·5 „	„	339·1 „	„
After explosion(dry).	289·2 „	„	203·9 „	„

These numbers give the following percentages by volume:—

	I.	II.	Mean.
CO ₂	0·08	0·11	0·10
O	20·97	20·97	20·97
N	78·95	78·92	78·93
	100·00	100·00	100·00

XII. Finally, a sample of air collected during the course of the experiments was submitted to analysis with the following results. An east or north-east wind prevailed during the whole time, and consequently the air at South Kensington had travelled across nearly the whole of London.

	Pressure.	Temp.	Pressure.	Temp.
Original gas (dry) ..	479.0 mm.	17.4°	734.4 mm.	18.1°
After absorption of CO ₂ (dry)	478.6 "	"	733.7 "	"
Ditto, new measurement for combustion (dry)	338.3 "	17.8	335.1 "	18.3
After admission of H (dry)	536.8 "	"	481.9 "	"
After explosion (dry).	324.1 "	"	271.1 "	"

These numbers give the following percentages by volume:—

	I.	II.	Mean.
CO ₂	0.08	0.09	0.09
O	20.94	20.95	20.94
N	78.98	78.96	78.97
	100.00	100.00	100.00

In the experiments with strong peaty water, the volume of air (corrected to 0° C.) contained in each bottle was 234.5 c.c., and from this the organic carbon alone in the water (0.00728 gram) would remove, during complete oxidation, 0.0194 gram or 13.5 c.c. of oxygen, leaving the residual air with only 15.1 per cent. of oxygen. Even a superficial inspection of the foregoing analytical numbers proves that in the most successful experiment in which the water travelled 20.4 miles in 10½ hours, whilst undergoing the most violent agitation with the enclosed air, there was but a very slight reduction of the proportion of atmospheric oxygen. Even in this instance, however, it is extremely unlikely that the oxygen thus absorbed was applied exclusively to the conversion of a minute fraction of the peaty matter into carbonic acid and water, and it is therefore almost certain that no trace of organic matter was really destroyed or "burnt up." Such portions as were attacked by the oxygen were only transformed into more highly oxidised forms of organic matter. Hence it follows that the slight excess of carbonic anhydride found in the residual air was derived from dissolved gases in the water and not from the organic matter, and this conclusion is confirmed, first, by the fact that in Experiments Nos. V, VII, and VIII, in which, as we shall show, the merest traces of oxygen were absorbed, the carbonic anhydride found in the residual air was even slightly greater than in Experiment VIII;

and secondly, because in Experiment IX, with the Kent Company's water, which certainly contains no spontaneously oxidisable organic matter, the proportion of carbonic anhydride found in the residual air was quite as high as in any other case.

Rejecting then the carbonic anhydride from the analytical results as of no import, we have the following proportions of oxygen and nitrogen in the residual air of the bottles and in the atmosphere of the laboratory in which all the experiments were conducted :—

	I.	II.	III.	IV.	V.	VI.
O	20·80	20·84	20·87	20·73	20·82	20·83
N	79·20	79·16	79·13	79·27	79·18	79·17
	100·00	100·00	100·00	100·00	100·00	100·00
	VII.	VIII.	IX.	X.	XI.	XII.
O	20·77	20·84	20·87	20·97	20·98	20·96
N	79·23	79·16	79·13	79·03	79·02	79·04
	100·00	100·00	100·00	100·00	100·00	100·00

If we compare the percentage amounts of oxygen found in the different samples of air which had been in contact with peaty water with those found in the air which had been similarly shaken up in the Kent and Colne Valley Companies' waters, and in the organically pure distilled water, and lastly with the percentage of oxygen in the air of the room in which the experiments were made, it is evident that minute quantities of oxygen have been absorbed by nearly all the samples of peaty water; but even in an extreme case, viz., the one in which the sample travelled more than 20 miles on the connecting rod of a steam-engine making 100 strokes per minute, the amount of oxygen absorbed by 250 c.c. of extremely peaty water was only 0·345 c.c., which is scarcely $\frac{1}{30}$ of that required for the complete oxidation of the organic carbon alone; or, in other words, only $2\frac{1}{2}$ per cent. of the organic matter was oxidised. Even this result is arrived at by the most favourable assumption, viz., that the whole of the oxygen taken up was employed in the oxidation of organic matter; but we have seen that even the Kent and Colne Valley Companies' waters absorbed oxygen, although they probably did not apply it to such a purpose. If we take only the oxygen absorbed by the peaty waters in excess of that taken up by these waters which probably contain no oxidisable organic matter, then only 1·6 per cent. of the organic matter could have been oxidised in the steam-engine experiment.

We conclude therefore that if peaty matter dissolved in river water is spontaneously oxidised at all (of which we consider there is as yet no sufficient proof), the process takes place with extreme slowness,

and cannot be accomplished to any considerable extent in the flow of a river: for our results show that peaty matter is even less oxidisable than animal matters under the same conditions.

During the experiments we noticed a considerable precipitation of brown peaty matter when the strong bog drainage was mixed with a comparatively small bulk of distilled water. We intend to investigate the cause of this precipitation, which promises to throw light upon the amelioration in peaty waters which has been observed by Mr. Bateman and other engineers.

XLI.—*On the Spontaneous Oxidation of Organic Matter in Water.*

By E. FRANKLAND, F.R.S.

CAN running water be at all times safely used for dietetic purposes a few hours or days after it has been mixed with sewage?—is a question of very vital importance to many millions of people in this country. Twelve years ago there was a general impression amongst chemists and others, that polluted water quickly regained its original purity by spontaneous oxidation. This opinion had no foundation in quantitative observations; indeed there was not a single experimental fact to support it, for the previous condition of water analysis did not permit of the quantitative investigation of organic matter dissolved in water. The impression had gained currency from the improved appearance of a polluted river after a flow of a few miles, and also from the disappearance of smell and blackness from putrescent water under similar circumstances. Two classes of persons, strongly interested in its acceptance, were chiefly instrumental in the origination and diffusion of this opinion. These were, first, polluters of running water; and secondly, water companies drawing their supplies below the sewer outfalls of towns. Both these influential classes, with enormous interests at stake, have always contended that even the most abominable of organic rubbish is destroyed by oxidation, in fact utterly “burnt up” during a flow of a few miles. There being no similarly organised opposition to the notion, the extensive credence which it gained from those who did not care much to investigate its truth, is not surprising. It was a comfortable doctrine, and therefore a popular one. Nevertheless it did not pass entirely unchallenged; indeed it is difficult to imagine how any chemist, accustomed to the habits of organic compounds, could accept such an opinion without the most conclusive proofs of its correctness. Thus in 1865 Professor Brodie entered his protest as follows:—

"I should say that it is simply impossible that the oxidising power acting on sewage running in mixture with water over a distance of any length is sufficient to remove its noxious quality. Taking the case of Oxford: If the sewage of Oxford was in its entirety discharged into the River Thames I should say that we could certainly not trust to the oxidising power to take away the noxious quality of the water before it reaches, say, Teddington. I presume that the sewage could only come in contact with oxygen from the oxygen contained in the water and also from the oxygen on the surface of the water; and we are aware that ordinary oxygen does not exercise any rapidly oxidising power on organic matter. * * * * We know that to destroy organic matter the most powerful oxidising agents are required; we must boil it with nitric acid and chloric acid and the most perfect chemical agents. To think to get rid of organic matter by exposure to the air for a short time is absurd."

And the first Rivers Pollution Commissioners,—Robert Rawlinson, Esq., C.B., C.E.; John Thornhill Harrison, Esq., C.E.; and Professor Way, state that "the river basin above Hampton comprises an area of about 3,676 square miles, and a population in 1861 of nearly 900,000 persons. After making every allowance for retention in cess-pools and for villages and houses situated within the limits of the basin, but removed from the banks of the river and its tributaries, there is no doubt that the number of persons whose sewage daily finds its way into the water from which London principally draws its supply amounts to hundreds of thousands, and this number is destined greatly to increase, not only by the growth of the population, but by the development of the sewerage system, now only in very partial operation. As the sewage travels down with the flowing water of a river a process of oxidation goes on which tends to purification. The volume of sewage is also small as compared with the volume of the river, and upon analysis the water pumped into London proves to contain only a very limited quantity of organic matter. But neither the one nor the other is a satisfactory ground of assurance that the metropolitan supply is wholesome. Sir B. Brodie's evidence is conclusive, that if the river be polluted with sewage at Oxford, the process of oxidation which the water more or less undergoes in its course is no sufficient guarantee of its arriving at Hampton purged of injurious sewage taint. The London drinker of Thames water may be drinking with it some remnant of the filth of Oxford. Again, it is the general opinion of medical men that what causes the presence of organic matter in water to be poisonous is not its quantity but its quality, and this special quality cannot as yet be detected by either microscope or chemical analysis, and is indeed at present known only by its occasionally noxious effects."

"The result seems to be that, as a water supply, the Thames, polluted with the sewage of the inhabitants of the river basin, is open in kind, if not in degree, to the same objections as well water infiltrated by liquid from an adjoining cesspool. Well water so tainted may appear to sight, taste, and smell to be harmless, and has been known to have been drunk for a length of time without apparent mischief, but beyond all doubt that same water is liable, under particular conditions, to become poisonous."

Notwithstanding its intrinsic absurdity, however, the prevailing opinion was in favour of the rapid oxidation of organic matter in running water when the second Rivers Pollution Commissioners of 1868 undertook, for the first time, the quantitative investigation of the subject. They continued it over a period of six years, and determined the rate of oxidation, first, during the flow of both intensely and moderately polluted rivers; secondly, in artificial mixtures of sewage and water by prolonged agitation with air; and thirdly, by observing the diminution of dissolved oxygen in a mixture of sewage and water excluded from the air.

All these experiments were conducted under my supervision, and all the samples were collected by me personally. The results were published in detail in the Sixth Report of the Rivers Commissioners, but I make no apology for bringing a summary of them before the Fellows of the Chemical Society, because they have not as yet appeared in any scientific journal.

Rate of Oxidation in Strongly Polluted Rivers.—For the determination of the rate of oxidation in strongly polluted water, the rivers Mersey, Irwell (a tributary of the Mersey), and Darwen (a tributary of the Ribble), were selected as streams offering favourable conditions for quantitative experiments; because, as I found by a minute personal inspection of each river, after being intensely polluted by organic matter, each of them flows for several miles without encountering any further material source of pollution. Moreover, and this is a most important condition, their waters are well mixed by falling over weirs or otherwise before what may be called the test-flow is entered upon.

The River Mersey, after receiving the drainage of many towns and manufactories above the Stretford Road Bridge, flows thence 13 miles to its junction with the Irwell without encountering any other material source of impurity, although its volume is augmented by unpolluted affluents. The River Irwell, after passing Manchester, falls over a weir at Throstlenest, and runs 11 miles to its junction with the Mersey without affluents. Lastly, the River Darwen, which was at that time greatly polluted by the sewage of Over Darwen, Lower Darwen, and Blackburn, joins the Blakewater just below the latter town, and then flows 13 miles to near its junction with the Ribble at Walton-le-Dale

without any further pollution, although its volume becomes more than double in this part of its course by the accession of the river Roddlesworth, the Alum House Brook, and numerous small affluents, all of which are unpolluted.

We took samples of the water of the rivers just indicated, viz.:—
1. The Mersey at Stretford Road Bridge, and again just before its junction with the Irwell. 2. The Irwell, just before it fell over the weir at Throstlenest, and again just above its junction with the Mersey; similar samples of this river being also taken in May and June following. 3. The Darwen, $\frac{1}{3}$ of a mile below its junction with the Blakewater, and again 50 yards above the bridge at Walton-le-Dale. The results of the analysis of these samples are contained in the following table (p. 521).

These numbers must not be interpreted too strictly, since it is evident that the proportions of the different constituents of river waters, so highly polluted as most of those experimented upon, must vary considerably from time to time at any given place in the stream. It is impossible to follow the same body of water for several miles down a river, because different portions of the stream in the same transverse section move with different velocities, and therefore no body of water included between two transverse sections of a river can retain its identity whilst flowing down the stream. It is thus very improbable that the sample of water taken, for instance, from the Irwell at its junction with the Mersey had, at the time when it fell over the weir at Throstlenest, the exact composition exhibited by the sample taken at that weir. Again, the entrance of unpolluted water into the rivers between the places whence the samples were drawn introduces another source of error which may be regarded as almost a vanishing quantity in the Irwell, considerable in the Mersey, but demanding correction in the Darwen, the volume of which was more than doubled by unpolluted affluents between the places of collection. Notwithstanding these complications, however, the above analytical results unmistakably disclose the effect of a flow of between 11 and 13 miles upon the quality of a polluted river. They show in the first place that even at the temperature of 18° C. such a flow produces but little effect upon the organic matter dissolved in the water, and that at and below 13° C. oxidation is practically arrested altogether; although in the case of the Irwell the water was most effectively aerated by falling over six weirs, a total height of $34\frac{1}{2}$ feet between the points where each pair of samples was collected, the river being covered with foam for several hundred yards below each weir. Making no correction for the unpolluted affluents of the Irwell and Mersey, and taking the volume of the Darwen to be only doubled between the points where the samples were taken by the accession of water containing

Results of Analysis Expressed in Parts per 100,000.

Description.	Matters in solution.						Suspended matters.			Temperature of water.		
	Total solid matters.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Chlorine.	Mineral.	Organic.		Total.	
March 12, 1869.	Irwell at Throstle-nest weir	44.6	2.104	0.248	0.230	0	0.437	7.4	1.84	0.96	2.80	6.2°
	Irwell at its junction with the Mersey	43.1	2.009	0.304	0.338	0	0.582	6.8	0.96	0.48	1.44	6.8
May 13, 1869.	Irwell at Throstle-nest weir	39.1	2.156	0.238	0.140	0	0.353	4.9	1.18	1.86	3.04	12.2
	Irwell at its junction with the Mersey	43.0	2.374	0.210	0.250	0	0.416	6.4	1.88	2.40	4.28	13.3
June 11, 1869.	Irwell at Throstle-nest weir, 8.30 a.m.	63.5	2.134	0.239	0.375	0	0.548	13.0	2.66	2.72	5.38	17.8
	Irwell at its junction with the Mersey, 6.10 p.m.	61.5	1.502	0.241	0.413	0	0.581	12.9	2.28	1.88	4.16	17.8
March 12, 1869.	Mersey at Street Road Bridge	19.8	0.720	0.095	0.066	0.022	0.171	2.3	0.94	0.30	1.24	4.3
	Mersey at its junction with the Irwell	22.8	0.570	0.078	0.043	0.019	0.132	2.5	0.84	0.26	1.10	4.8
March 10, 1869.	Darwen after junction with Blake-water	41.5	2.127	0.295	0.219	0	0.475	3.6	1.78	1.78	3.56	10.7
	Darwen at Walton-le-dale	33.0	1.289	0.141	0.137	0.045	0.299	2.9	0.62	0.18	0.80	6.8

the proportions of organic carbon and nitrogen present in the Ribble just before its junction with the foul water of the Darwen, viz., 0·327 part organic carbon and 0·026 part organic nitrogen in 100,000 parts, we have the following reduction in these elements of organic matter in the five experiments:—

				Percentage reduction of organic elements.
1.	Irwell, after flow of 11 miles, at	6·5° C.	1·7
2.	„ „ „	12·7	„	0
3.	„ „ „	17·8	„	26·5
4.	Mersey „ 13 miles, at	4·5	„	20·5*
5.	Darwen „ „	8·7	„	0

Rate of Oxidation in the Thames at Reading.—The rivers Irwell, Mersey, and Darwen are notoriously much polluted by sewage and other refuse organic matters. So intense indeed is their pollution that ordinary aquatic life is entirely banished from their waters. We deemed it therefore desirable, in order to complete this part of our investigation, to ascertain the effect of a flow of some miles upon the water of a river less polluted and in which animal and vegetable life still flourished. For this reason we selected the Thames between Reading and Shiplake Paper Mill. Just below Reading the Thames receives an important affluent, the Kennet, but it then flows about four miles without receiving any other affluent or pollution of importance. We collected samples of the water about a quarter of a mile below the junction of the Kennet, and again just above Shiplake Paper Mill, and submitted these to analysis with the following results:—

Results of Analysis Expressed in Parts per 100,000.

Description.	Matters in solution.						
	Total solid matters.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Chlorine.
The Thames $\frac{1}{4}$ mile below junction with the Kennet, 2 p.m. May 31st 1873	28·86	0·261	0·071	0·007	0·167	0·244	1·70
The Thames just above Shiplake Paper Mill 5.48 p.m. May 31st, 1873	28·42	0·245	0·068	0·007	0·155	0·229	1·70

* No correction for unpolluted affluents.

Results of Analysis expressed in parts per 100,000 (continued).

Description.	Suspended matters.			Temperature of water.
	Mineral.	Organic.	Total.	
The Thames $\frac{1}{4}$ mile below junction with the Kennet, 2 p.m. May 31st, 1873.....	0·42	0·06	0·48	16·7°
The Thames just above Shiplake Paper Mill, 5.48 p.m. May 31st, 1873	0·14	0·10	0·24	16·7°

It is obvious that for a just comparison in such cases the samples must be collected with every care and precaution. I have had continued occasion to observe that when an affluent joins a quietly flowing river, the tributary and main stream flow side by side for a long distance without admixture. I have thus seen the Thames and the Kennet after their junction, when the latter stream has been turbid and the former clear, flowing without any perceptible mingling for more than a quarter of a mile, and it is almost certain that these rivers do not get thoroughly mixed until they reach the weir and rapids at Sonning Bridge, nearly two miles below their junction. *Any sample taken from either shore, between the point of junction and Sonning Bridge, would therefore certainly not represent the average composition of the whole stream,* and it thus became necessary to take the higher sample in small fractions whilst crossing the river in a boat. To secure a correct comparison it was necessary to make the interval between the two samples correspond approximately with the time of flow of the river between the two points at which they were taken. These precautions were duly observed; and, moreover, the trial was made on a bright sunny day at the end of May, when aquatic life had a maximum of activity. The analytical results embodied in the foregoing table show that even under these very favourable circumstances, the reduction in the proportion of organic matter was exceedingly small, being only 5·7 per cent. at the temperature of 16·7° C.; so minute, indeed, that even assuming it to go on at the same rate by night and day, in sunshine and gloom, it would require a flow of 70 miles to destroy the organic matter present in the Thames after its junction with the Kennet. We know, however, that the removal of organic matter from the water would go on much more slowly in the shade, and would be almost arrested during the night; so that it would be incorrect to assume that the river would clear itself of organic matter by a flow of 70 miles.

Rate of Oxidation when Polluted Water is strongly Agitated with Air.

—In order to check any uncertainty attaching to the foregoing results by reason of the variability of the composition of river water, an artificial mixture of London sewage and clean water of known composition was made. It was violently agitated in contact with air every day, besides being always kept in an open glass vessel, from which it was daily syphoned off in a slender stream, falling through 3 feet of air, and broken up for the most part into separate drops, the temperature of the air being about 20° C.

The mixture contained at the commencement in 100,000 parts, 0·267 part of organic carbon, and 0·081 part of organic nitrogen. After 96 hours it still contained 0·250 part of organic carbon, and 0·058 part of organic nitrogen, and even after 192 hours the unoxidised organic matter still contained 0·200 part of carbon, and 0·054 part of nitrogen.

These results show that in 96 hours the organic carbon was reduced by 6·4 per cent., and the organic nitrogen by 28·4 per cent., whilst after 192 hours, the reduction was 25·1 per cent. of carbon, and 33·3 per cent. of nitrogen, and as the mixture was at least as much exposed to the air as it would be in a flowing river, it may be fairly assumed that this amount of oxidation would, at the same high temperature, be produced by a flow of 96 and 192 miles respectively at the rate of 1 mile per hour.

A similar set of experiments was made with a mixture of fresh human urine, and the deep chalk well water supplied to London by the Kent Water Company, in the proportion of 1 gallon of urine to 3,079 gallons of water. The mixture was exposed to the air, and briskly agitated as before. A sample of it was submitted to analysis immediately after mixture, and samples were taken and analysed at almost daily intervals afterwards. The results of these analyses are embodied in the following table:—

				Org. carbon.	Org. nitrogen.
Immediately after mixture, February					
17th, 1874			0·282	0·243
After 1 day on February	18th, 1874			0·298	0·251
„ 2 days	„ 19th	„		0·244	0·255
„ 7 „	„ 24th	„		0·225	0·253
„ 8 „	„ 25th	„		0·214	0·259
„ 11 „	„ 28th	„		0·214	0·276

To guard against the introduction of any error into these results by the access of atmospheric dust during the prolonged agitation of the mixture, a similar volume of the Kent Company's water, without any admixture of urine, was treated in the same way; 100,000 parts of it contained at the commencement 0·054 part of organic carbon, and

0·016 part of organic nitrogen, whilst after 11 days' agitation, the organic carbon and nitrogen amounted to 0·056 and 0·017 part respectively.

The water, therefore, abstracted but the merest traces of organic matter from the air, and the results show that fresh urine undergoes even a slower oxidation than sewage. But it must be remembered that the temperature during these last experiments was probably lower, as they were conducted in winter. Flowing at the rate of 1 mile per hour in a river, the mixture experimented upon would travel over 264 miles before it would lose by oxidation 7 per cent. of its organic constituents.

Rate of Disappearance of Dissolved Oxygen.—There is yet another method calculated to contribute to the solution of this problem, viz., the study of the rate at which atmospheric oxygen disappears when dissolved in organically polluted water. A quantity of sewage water, containing in 100,000 parts, 2·099 parts of organic carbon, and 0·207 part of organic nitrogen, was put into a series of accurately stoppered bottles, which were exposed to diffused daylight, and kept at a temperature of about 17° C. One of them was opened every 24 hours, except on an intervening Sunday, and the weight of dissolved oxygen contained in the enclosed water determined by boiling off the dissolved gases in a vacuum. It was found that before the sewage water was put into the bottles, 100,000 parts of it contained 0·946 part by weight of oxygen. A bottle opened after 24 hours, contained 0·803 part; another after 48 hours, 0·616 part; after 96 hours, 0·313 part; after 120 hours, 0·201 part; after 144 hours, 0·080 part; and after 168 hours, 0·036 part.

These numbers confirm the results previously recorded. They show that even in warm weather, the oxidation of the animal organic matter in sewage takes place very slowly. Leaving altogether out of the question the oxidation of the hydrogen and nitrogen, and assuming that for the destruction of the organic matter, the carbon alone requires to be oxidised (3 parts by weight of carbon requiring for this purpose 8 parts of oxygen), then the percentage of sewage destroyed in each of the above periods will be as follows:—

Percentage of sewage destroyed.				
1st period of 24 hours . . .				6·8
2nd " 24 " . . .				8·9
3rd " 48 " . . .				14·3
4th " 24 " . . .				5·4
5th " 24 " . . .				5·8
6th " 24 " . . .				2·1
				<hr/> 43·3

Up to the end of the sixth day (or 5th period) the oxidation took place at a tolerably constant, though somewhat diminishing rate; the amount of oxygen still left in solution had, however, then become so small as greatly to retard the rate during the next 24 hours, when the experiment was discontinued. Assuming, however, that if the polluted water had been constantly exposed to the air, a portion at least of the oxygen used would have been replaced; and assuming further that the oxidation proceeded during 168 hours, at the maximum rate observed, then at the end of that time only 62·3 per cent. of the sewage would be oxidised. But even this result is arrived at by a series of assumptions, which are greatly in favour of the efficiency of the oxidising process. Thus, for instance, it is assumed that the 62·3 per cent. of sewage was thoroughly oxidised and converted into inoffensive inorganic matter, but the experiments showed that in fact no sewage whatever was so converted or destroyed, even after the lapse of a week, since the amount of carbonic acid dissolved in the water remained constant during the whole period of the experiment; whilst if the sewage had been converted into inorganic compounds, the carbonic acid, as one of these compounds, must have increased in quantity.

Upon these results the Rivers Commissioners remark as follows:—

“Thus, whether we examine the organic pollution of a river at different points of its flow, or the rate of disappearance of the organic matter of sewage or urine, when these polluting liquids are mixed with fresh water, and violently agitated in contact with air; or, finally, the rate at which dissolved oxygen disappears in water polluted with 5 per cent. of sewage—we are led in each case to the inevitable conclusion that the oxidation of the organic matter in sewage proceeds with extreme slowness, even when the sewage is mixed with a large volume of unpolluted water, and that it is impossible to say how far such water must flow before the sewage matter becomes thoroughly oxidised. It will be safe to infer, however, from the above results, that there is no river in the United Kingdom long enough to effect the destruction of sewage by oxidation.”

These experiments and observations have never been called in question during the six years which have elapsed since their publication; but Dr. Tidy, in a paper on River Water, which he communicated to this Society in March last, whilst conceding their accuracy, objects to the conclusions drawn from them, and describes the results of other experiments recently made by himself, which, in his opinion, demonstrate that peaty matter is very rapidly, and sewage still more rapidly, oxidised in running water. These experiments induced him to make the following statement:—“I am led to the inevitable conclusion that the oxidation of the organic matter in sewage, when mixed with unpolluted water and allowed a certain flow, proceeds with *extreme rapidity*,

and that it is impossible to say *how short a distance* such a mixture need flow under favourable conditions before the sewage matter becomes thoroughly oxidised."

This conclusion is founded upon the results of analyses of water taken from the Severn, the Shannon, and from certain conduits belonging to a waterwork in the north of England, as also upon experiments made with sewage water flowing through glass troughs. A careful examination, however, of the conditions under which the samples were taken and the experiments made, shows that they are, in most cases, quite consistent with my own results, and that not one of them affords any trustworthy basis for the conclusion the author arrives at.

From the Severn, samples were collected in January, 1878, at various places from Worcester, above the sewer outfall, down to Tewkesbury, a distance by river of 16 miles. The composition of the Teme, which is the largest feeder of the Severn, and joins the river in this part of its course, bringing down a great body of very pure water, was also ascertained. The river was 18 inches above mean ordinary level, and the water had a mean temperature of 7.5°C . It would, in my opinion, have been difficult to select a stretch of river more unfavourable for the study of oxidation. First, the sewage of Worcester is poured into it, then two miles below Worcester Bridge the river is joined by the Teme, which, according to the author's analyses, is organically nearly *nine times* as pure as the Severn where they meet.

The taking of fair average samples of water from rivers receiving numerous affluents of very different composition is extremely difficult, if not impossible. Every traveller up the Rhine knows that the yellow muddy water of the Main does not mix with the blue of the Rhine until they reach the rapids in the Binger Loch, 20 miles lower down; and, on a much smaller scale, I have watched a muddy feeder run, under favourable circumstances, for a mile or two alongside the clear water of the main stream. Under such conditions the only way to obtain an approximately average sample is to cross the river in a boat, to take specimens every yard or so, and then to mix them all together.

If the Severn samples prove anything about oxidation, they prove too much: for comparing sample No. 2 with sample No. 3, both taken just below Worcester (see p. 283), it appears that a flow of 30 yards reduced the organic elements in 100,000 parts of the water from 1.103 to 0.751 or 32 per cent. *At this rate the Severn would be absolutely free from organic matter before it covered the distance of 100 yards*, and it is therefore somewhat disappointing to find that after a further flow of a mile, it had scarcely lost 12 per cent. more. It is evident that the sewage

of Worcester had not mingled with the Severn water in the flow of a mile, and Dr. Tidy does not appear to have taken the precautions just mentioned, and which were observed by me on the Thames, to secure fair average samples across the river. His analyses, in fact, illustrate nothing about oxidation; they show only the gradual mingling of the sewage with the main stream. That this is the true interpretation of them is confirmed by reference to the chlorine determinations. The sample taken near the mouth of the sewer outfall contained 4.752 grains of chlorine per gallon; the next sample 30 yards lower contained only 2.808 grains per gallon, or 41 per cent. less; the next sample, one mile below Worcester Bridge, contained only 2.448 grains, showing a further reduction of 8 per cent. These reductions of chlorine proceed *pari passu* with those of organic elements: for whilst the chlorine is diminishing by 41 and 8 per cent., the organic elements decrease by 32 and 12 per cent. If the organic elements diminish by oxidation, what is the nature of the chemical process which removes the chlorine? This diminution of chlorine does not escape Dr. Tidy's notice. He says: "The diminution of chlorine in a sewage-polluted water after a certain run, until it assumes the normal of 1 grain or thereabouts per gallon, is interesting. Probably the excess of chlorine, which is brought into the river by the sewage, *is taken up by vegetation.*" No proof of this statement is offered, neither is there any estimate made of the amount of vegetation which would be necessary to remove nearly half of the chlorine from Severn water during a flow of 30 yards. I venture to affirm, however, that there is no such process, and these chlorine determinations conclusively show that the sewage of Worcester was gradually mingling with the Severn water which contained, just above Worcester, only 2.304 grains of chlorine per gallon.

Similarly, the samples taken below the junction of the Teme illustrate, not oxidation, but the gradual mingling of the pure water of the Teme with the polluted water of the main river: for, according to Dr. Tidy's analyses, the organic matter goes on increasing the further the river flows. Thus, a quarter of a mile below the junction, the proportion of organic elements is only 0.137 per 100,000, whilst at four miles below the junction it has increased to 0.212, at six miles to 0.215, and at Tewkesbury to 0.230 part per 100,000. The chlorine determinations again show the same thing (except that there is a slight diminution at Tewkesbury), the simple and obvious cause being that the water of the Teme, with only 0.072 part per 100,000 of organic elements and 0.648 grain of chlorine per gallon, is gradually mixing with the Severn, containing nearly ten times as much organic matter and four times as much chlorine. The author, however, is not content with this explanation. In the case of the River Wear, where the reduction in the

amount of chlorine was a difficulty in the way of his assumption of oxidation, he invents the hypothesis of the absorption of chlorine by aquatic vegetation. In the case of the Severn, the augmentation of chlorine has to be accounted for, and the author at once creates brine springs at the bottom of the river.

Let us now take the case of the Wear, which he adduces as a most convincing proof of oxidation; and, with his description alone before us (*see* page 305), it must be admitted that the evidence is overwhelming. Between Bishop Auckland and Durham "the sewage of about 100,000 people" enters the previously unpolluted river. Two hundred yards below Bishop Auckland, "the river water (presumably on the side of the sewer outfall) was manifestly sewagey, the banks were dirty, the water turbid, and vegetation sparse. The organic carbon had risen to 0.260 and the organic nitrogen to 0.070 part per 100,000."

"After a flow of half a mile, the blackness of the river disappeared, whilst at Durham, a distance of but 13 miles from Bishop Auckland, the river water showed a far greater degree of purity than even above the sewer outfall at Bishop Auckland. * * * Not merely is the whole of the sewage of Bishop Auckland (and any other sewage that finds its way into the river) *oxidised* in the course of the run, but some of the organic matter that was in the river before it reached Bishop Auckland is also oxidised." Such is the energy of oxidation in this river, that even the nitrates themselves appear to be oxidised, for none are to be found in the river at Durham. Lastly, the Rivers Pollution Commissioners are made to testify that the Wear at Durham is "*a good water*." These statements seem very conclusive, and yet the conclusion drawn from them by the author is utterly unwarranted, and is tenable only by keeping out of view the fact that between Bishop Auckland and Durham the river receives a considerable ferruginous tributary, containing no less than 9.43 parts of metallic iron in 100,000 parts.

The author surely cannot be ignorant of the potency of iron in various forms for the removal of organic matter from water. At pages 5 and 6 of the Fifth Report of the Rivers Commissioners, this purifying action of ferruginous colliery water is abundantly illustrated in the Calder at Todmorden, the Taff below Merthyr, and the Wear above Durham. Writing of the ferruginous drainage from collieries, the Commissioners say: "One of the most characteristic streams of this kind that we have seen runs into the Wear a few miles above the point where the Durham Water Company pump their water from the river. It is as red as any mining river in Great Britain, depositing an orange-coloured mud, which heightens the bright-red colour of the turbid water passing over it. It joins the Wear on its right bank near Croxdale Hall, *just opposite the junction of the Brownie*, a clean

and much larger affluent on the other side. Judging from temperatures taken of the three streams and of the Wear above and below their junction with it, this red stream is not more than one-thirtieth of the whole volume of the united waters, but the water of the Wear, bright and colourless as it appears from Sunderland Bridge, half a mile above this junction, has become yellow and turbid at Butterby, a mile below it. Tracing the stream upwards through the 8 or 10 miles of its course, we find it red to its very source. Its head waters are pumped from the East Hetton, Kelhoe Winnings, and Coxhoe Collieries, which lift 400, 1,100, and 900 gallons a minute respectively. Samples of these waters contained the following quantities of iron in solution :—

	Metallic iron in 100,000 parts.
Red stream running into the Wear between Bishop Auckland and the intake of the Durham Water Company	9.43 parts.
Water pumped from Kelhoe Winnings Coal-pit	25.30 „
Water pumped from 60 fathom working of East Hetton Colliery	8.92 „

It is therefore evident that the author has again been unfortunate in his selection of the Wear for proof of oxidation during flow. River water loses nearly the whole of its organic matter by brief contact with spongy iron, and the lower oxides of iron act in a similar manner; but whatever may be the explanation of this phenomenon, no one will allege that the cleansing is effected by oxidation.

The quotation italicised by Dr. Tidy from the Sixth Report of the Rivers Commission, "*a good water*," is, as I think the author will admit on reconsideration, scarcely a fair one. In the first place, the quotation does not refer to the river Wear water at Durham, as stated in Dr. Tidy's paper, but to the water of the Wear at Shincliffe, *after filtration* through the unusual thickness of 9 feet of sand and grit. What the Rivers Commissioners really did say about the Durham water supply will be seen from the following more complete quotation to be very different from the commendation which Dr. Tidy's quotation might be supposed to imply :—

They say (6th Report, p: 338): "The river is stated to be polluted by 'hush'—the *débris* from the washing floors of lead works—and by sewage from Bishop Auckland and other small towns higher up the stream. There was, however, but small evidence of this pollution in our sample, which shows the water to have been on that occasion of good quality, *considering its source*. Indeed, a comparison of the water, before and after filtration, indicates a much greater improvement than is usually effected by that process, which is perhaps accounted for by

the circumstance that the filters are of the unusual depth of 9 feet. The filtering medium is composed of a layer of broken grit stones 2 feet deep, fine layers of coarse and fine gravel each 6 inches deep, and a layer of clean-washed river sand 4 feet 6 inches deep. Although we do not consider that water taken from a river subject to direct sewage contamination is a safe supply for a town, yet it is greatly to be preferred to that of the shallow wells of the city, if the well of the Medical Officer be, as described to us, one of the best. This water, though clear and sparkling, is shown by our analysis to be little else but the percolations from sewers and cesspits; 100,000 lbs. of it contain the inorganic remains of as much excrementitious matter as is present in 62,360 lbs. of London sewage."

Dr. Tidy also refers to the Thames as an illustration of oxidation by flow, but as he brings forward no new facts, I need not enter into this instance in detail, especially as it has already received a good deal of attention. This river is not well adapted for the study of oxidation by flow in any part of its course, but it lends itself most readily to the support of *ad captandum* arguments about oxidation. It starts on its course at Lechlade, 'having assumed (as the author expresses it) as nearly as possible the character of river water,' and containing, in his opinion, at this point no sewage. Then it receives 'the sewage of nearly a million people,' but arrives at the intakes of the water companies at Hampton slightly purer than when it started. And then it is triumphantly asked, what had become of the sewage of this million people if it had not been oxidised during the flow of the river?

This question could not be fully answered within the limits of this paper, but I may be permitted briefly to glance at one or two of the data involved in the answer. In the first place, what is the evidence that Thames water contains less organic purity at Hampton than at Lechlade? The only evidence bearing upon the organic condition of the river at these two points of its course is furnished by two samples of water, taken by Dr. Pole for the Royal Commission on Water Supply, and analysed by Dr. Odling and myself. These analyses gave the following proportions of organic elements in 100,000 parts:—

	Organic carbon.	Organic nitrogen.
The Thames at Lechlade, April 18th, 1868 ..	0.133	0.033
The Thames at Hampton, May 4th, 1868 ..	0.260	0.024

These results were obtained with samples taken, it will be observed, 16 days apart, the Lechlade sample being a portion of the river running at the time, according to the estimate of Dr. Pole, C.E., 100,000,000 gallons daily; whilst the Hampton sample formed part of

the river where it was running, on the day when it was collected (according to the gaugings of Mr. John Taylor, C.E.), at the rate of 554,000,000 gallons daily. When, moreover, it is considered how great may be the variations in the constituents of a river like the Thames in the course of 16 days (there was in fact a flood in the Thames, beginning on April 21st, and continuing until the 24th), it is evident that those samples are in no way comparable. But even granting that the Thames at Hampton contains, in dry weather, no more organic matter than the Thames at Lechlade, it by no means follows that the sewage of a million people has been got rid of by oxidation in the river; for, in the first place, the volume of the Thames is augmented between the two points more than five-fold, and much of this additional water in dry weather enters the river as spring water, containing only about one-fourth the organic matter present at Hampton.

Secondly, it certainly is not the fact that one million people drain into the Thames and its tributaries, *in dry weather*, between Lechlade and Hampton. A considerable proportion of this population drains into cesspools, which do not overflow in dry weather; and as regards the sewage of the remainder, a large quantity of filth stagnates in sewers and house drains, until a fall of rain flushes it out into the river. Thus it is that with an enormously augmented volume of water, the proportion of organic impurity in the flood waters of the Thames at Hampton is increased many fold. The sewage of days, or even weeks accumulates, and is kept out of the Thames in dry weather to be swept into the river by the next considerable rainfall. The very different story told by the river when the sewers and cesspools are kept regularly flushed, in nearly continuous wet weather, is well seen in the condition of even the filtered Thames water supplied to London during the months from May to October, inclusive, of the year 1879; when, with an enormously increased flow, the proportion of organic elements averaged nearly three times that found in the much smaller volume of Thames water in dry seasons. It is in the flood waters of the Thames that a good deal of the sewage of the million people is to be looked for!

Thirdly, it was pointed out by Dr. Odling and myself, in a report to the Royal Commission on Water Supply (Appendix to the Report of the Royal Commission on Water Supply, p. 119), that when Thames water is mixed with the water of the Wey, which joins the Thames six miles above Hampton, the mixture becomes perceptibly turbid, and a precipitation of organic matter takes place, amounting to 0.037 part of organic elements in 100,000 parts of water. There is therefore another process quite independent of oxidation, tending to diminish, though only to a slight extent, it is true, the proportion of organic matter in river water.

Fourthly, for several miles above Hampton, the Thames runs through a vast deposit of flint-gravel and sand, which sops up its water like an immense sponge, restoring it again to the river, either near the place of absorption after floods, or below the next lock in dry weather. Thus vast volumes of Thames water are purified by this exhaustive filtration through gravel and sand, that is to say, by oxidation in a porous medium, which I have again and again shown to be the most potent agency in nature for the removal of organic matter from water. The Lambeth Water Company has for some time past availed itself of this naturally filtered Thames water, which is obtained at its new works at West Moulsey, by laying perforated mains along the foreshore of the Thames, and pumping from these into the reservoirs. The great improvement thus effected in the quality of the water is seen from the following comparative analyses (made by Dr. Tidy, Dr. Voelcker, and myself) of water taken simultaneously from the Thames and from the perforated mains in the Lambeth Company's works*.

Results of Analysis Expressed in Parts per 100,000.

Description.	Total solid matters.	Organic carbon.	Organic nitrogen.	Ammonia.	Nitrogen as nitrates and nitrites.	Total combined nitrogen.	Chlorine.
The Thames off Lambeth Company's works at West Moulsey, March 13th, 1880 } Water pumped from gravel at Lambeth Company's works, March 13th, 1880	31·16 33·32	0·261 0·127	0·045 0·041	0·004 0·004	0·186 0·213	0·234 0·257	1·5 1·5
The Thames off Lambeth Company's works, April 5th, 1880 } Water from gravel at Lambeth Company's works, 5th April, 1880.....	27·39 31·27	0·225 0·155	0·068 0·021	0·009 0·007	0·217 0·265	0·288 0·289	1·3 1·6

* Evidence of this improvement is not to be found in my monthly reports to the Registrar-General on the Thames waters supplied to London, because the purified water is transmitted from West Moulsey to Thames Ditton, a distance of about three miles, chiefly through a brick culvert, in which it contracts so much organic impurity as completely to neutralise the advantage of this natural filtration.

Results of Analysis expressed in parts per 100,000 (continued).

Description.	Hardness.		
	Temporary.	Permanent.	Total.
The Thames off Lambeth Company's works at West Moulsey, March 13th, 1880	13·8	7·4	21·2
Water pumped from gravel at Lambeth Company's works, March 13th, 1880.....	14·2	7·0	21·2
The Thames off Lambeth Company's works, April 5th, 1880	16·0	5·7	21·7
Water from gravel at Lambeth Company's works, April 5th, 1880	15·6	8·3	23·9

There can be no doubt, therefore, that oxidation in this bag of gravel is a very potent cause of the exceptionally low proportion of organic elements in Thames water about Hampton.

I now turn to Dr. Tidy's observations on the Shannon, which were made at a time when the river was 2 feet above ordinary summer level. Samples were collected from the head of Lough Derg down to $1\frac{1}{2}$ mile above the town of Limerick; but as the river receives an important tributary, the Mulkear, $2\frac{1}{2}$ miles below the Leap of Doonass, and, as the author shows that the suspended mineral matters in this river exert a very powerful influence, quite independent of oxidation, in removing soluble peaty matter from the Shannon, the observations on oxidation were limited to a stretch of 37 miles, of which 23 were in Lough Derg, and 14 in the river.

According to Dr. Tidy's analyses (p. 285) the Shannon, in flowing through Lough Derg (2 miles of river and 23 of lake), suffers a reduction of its organic elements from 1·02 to 0·84, that is to say, not quite 18 per cent., the samples being taken at Portumna Bridge, above the inflow, and at Killaloe, below the outflow. The next sample, taken a mile below the previous one, shows a reduction of 0·324 part of organic elements per 100,000, or more than 38 per cent. The next sample was procured at O'Briensbridge, 4 miles lower down, and this shows an increase of 0·384 part, or nearly 75 per cent. of organic elements. About 4 miles below O'Briensbridge the river falls 50 feet at Doonass Leap, or Castle Connell Falls, and the next sample was taken a little below the foot of these falls. It showed, in comparison with the last, a reduction of 0·257 part, or more than 28 per cent. of organic elements. The last sample of the series illustrating oxidation

was taken above the junction of the river Mulkear, and, I presume, about two miles below the place where the previous sample was obtained. Here the organic elements had again increased by 0.341 part per 100,000, or 53 per cent.

A series of analyses showing such sudden bounds, alternately upwards and downwards, in the proportion of organic elements, seems to me ill-adapted for the proof or disproof of oxidation; but when we examine these changes in detail, it is seen that the use made of them by the author is utterly out of the question. In the first place we are asked to believe that a run of only one mile in the Shannon reduces, by oxidation, the organic elements to the extent of more than 38 per cent., whilst the passage of 23 miles through Lough Derg, plus *two* miles of river, occupying many weeks, if not months, diminishes them by scarcely 13 per cent. Now Lough Derg exposes to the air, according to the Ordnance Survey, a surface of no less than 51.2 square miles (this surface being kept in almost constant agitation by the wind), and receives, during the time the river is passing through it, a not inconsiderable quantity of rain water; whilst the one mile of river has a surface of less than one-tenth of a square mile, and the water is not, I presume, exposed to the air for more than one hour in making the transit; and there are, I believe, no falls in this part of the river. The author is evidently dissatisfied with the comparatively slight effect of 25 miles flow through Lough Derg, for he says,—“A large quantity of peaty land drains into it; hence the difference in the quantity of organic carbon found in the water collected at the south of the lake over that found in the water collected at the north, in no way expresses the actual quantity of peat oxidised during the passage of the water through the lake.” A “large quantity of peaty land” is a somewhat vague term: but, with the exception of a considerable stream running into Stonysland Bay, at the head of the lake, the Ordnance map shows few tributaries of importance; for the Shannon basin is here somewhat narrowed, and the streamlets, some of which are dignified by the name rivers, run a course of only a few miles into the lake. As a set-off to this, however, the author tells us that the quantity of bog drainage finding its way into the one mile stretch of river below Killaloe “is not inconsiderable.”

Leaving this oxidising section, the Shannon flows four miles to O'Briensbridge, and more than regains all the organic matter it is alleged to have lost in that wonderful mile below Killaloe, no less than 75 per cent. of peaty matter in solution being added in the run. In this stretch, the Ordnance map shows four streams entering the river on the right bank, and four on the left. Of these four have a run of less than two miles, and, of the remainder, although one has the ominous name of “Black River,” there are none drawn with a double

line on the Ordnance sheet, and this shows that they are inconsiderable streams. Now the author says (page 294), "If the water contains 1 grain of peat per gallon, the 2-foot tube shows it of a *porter* tint. If the water contains 2 grains of peat per gallon, the 2-foot tube shows it as *black*." It must be remembered that the blackness produced in a 2-foot tube is equivalent to that of the same water 1 foot deep in a river or lake, even if the bottom were white, and of course to much less depth if coloured. Since dry peat contains 60 per cent. of carbon, these numbers correspond to 0.857 part, and 1.714 part of organic carbon, in 100,000 parts of water. Taking the higher of these numbers as the proportion of organic carbon contained in the peaty streams entering the Shannon in this five-mile reach (the author gives no analysis of any of these streams), it follows that to raise the organic carbon from 0.48—the proportion found at the top of the reach—to 0.84—the amount obtained at O'Briensbridge, the volume of the Shannon must have been augmented by peaty affluents to the extent of considerably more than one-third, or, more correctly, every $2\frac{3}{4}$ volumes of Shannon water must have become mixed with 1 volume of the black peaty water. When it is remembered that the Shannon drains one-fourth of Ireland, and is one of the largest rivers in the United Kingdom; that the rainfall on the upper part of its catchment basin is between 40 and 50 inches per annum; that the river was in flood and near the end of its course when the samples were taken; and lastly, that there is no considerable affluent in this part of its run, it is impossible to believe that the river received even one-tenth part of the required volume of black water during its flow along the five miles in question. Lower down again we have to contend with the same difficulty, for in a run of only two miles from the foot of Doonass Falls to the junction of the Mulkear, we have again, according to the author's analyses, an increase of 53 per cent. of organic elements, calling for another addition of more than one-third of black peaty water to the volume of the main stream, although the Ordnance map ignores any addition beyond two minute streamlets. But how are these fluctuations in the composition of the samples to be accounted for? It is scarcely my province to answer this question, as I was not present when the samples were taken. I have the fullest confidence in Dr. Tidy's analytical results, but I have no faith whatever in the samples taken one mile below Killaloe and Castle Connell respectively, truly representing the average composition of the river at those points. There can be little doubt that here, as in the Severn, the influx of affluents affected samples taken from the shore, and I would point out that immediately above the spot, one mile below Killaloe, there are two tributaries entering the Shannon through the left bank, and, as the only road runs along this bank, I presume the sample at the end of the one-mile flow

was taken from this shore. There is also a tributary which enters on the same side, one mile below Castle Connell, and therefore just about the place where the second sample of so-called oxidised water was obtained; and here again the only road is on the same side as the tributary. That water foreign to the Shannon was included in this last sample is certain, from the sudden rise in the total solid matter from 17.30 to 20.2 grains per gallon.

Now the Ordnance map indicates that there is but little peat on this side of the river, and the analysis of the Mulkear water shows that this river, although it drains the most boggy area to the left of the Shannon, is very much less peaty than the main stream. It contained in fact only 0.212 part of organic carbon per 100,000 parts. If the other streams entering the river on the same shore possess this degree of purity, then the reduced amounts of organic carbon found in the samples taken immediately below their junction with the main stream and from the same shore need excite no surprise, as the purest of them contains more than twice as much organic carbon as the Mulkear water. Rejecting, then, as abnormal, the two samples taken one mile below Killaloe and Castle Connell respectively, we have the following series:—

	Distance from Portumna.	Organic elements in 100,000 parts.
Shannon at Portumna north of } Lough Derg..... }	—	1.020
Ditto at Killaloe, south of } Lough Derg..... }	25 miles	0.840
Ditto at O'Briensbridge.....	5 „	0.900
Ditto above junction with } River Mulkear..... }	7 „	0.984

Whatever interpretation may be put upon these analytical data, it is quite obvious that, below the lough at all events, they afford no support to the theory of oxidation. Neither can the samples from the north and south ends of the lough be used for this purpose, because the water issuing from Lough Derg probably entered that lough at least a month previously, and we know absolutely nothing of the proportion of organic matter contained in it at that time. Consequently the two samples are not comparable with each other.

As regards Dr. Tidy's analysis of peaty water from an open and a closed conduit fed from the same reservoir (p. 297), apparently showing oxidation of organic matter in the open conduit and none in the closed pipe, I submit that the results obtained by Miss Halcrow and myself on the behaviour of peaty water in contact with air (see p. 516) show that here again, whilst fully recognising the accuracy of Dr. Tidy's experimental results, there must have been some fallacy in

the samples. What the fallacy is in this case it is obviously impossible for me to point out without visiting the waterworks in question and making a careful inspection of the conduit, but I am convinced that the smaller proportion of peaty matter in the open conduit water is due to other causes than oxidation simply by flowing in contact with air—probably to the admission of spring water *en route*, or to the large surface of rough brickwork in contact with a small stream of peaty water. There is no evidence that the brick conduit did not receive spring water in its course of 6,820 yards. The author gives no other constituent except the organic carbon. The volume of water running down the conduit ought also to have been mentioned, for a slight flow of water over a rough surface of brickwork would be a near approach to percolation through a gravelly soil. That a large volume of water passing through a brick conduit for less than four miles should have its organic carbon reduced to one-half is contrary to all my experience, and is simply incredible; but if true the discovery would be invaluable to many water companies.

Moreover, if dissolved oxygen is so active in destroying organic matter, how was it that the water flowing the same distance through the closed pipe not only exhibited no diminution of organic carbon, but even a small increase? Like all such water, it was doubtless saturated with atmospheric air containing 33 per cent. of oxygen, and yet we are asked to believe that so long as the water remained in a closed main its organic matter suffered no oxidation. Was not the non-disappearance of organic carbon in this case due to the exclusion of purer water in transit? In an experiment of my own, the East London Company's water, entering their main at Sunbury, containing 0.159 part per 100,000 of organic carbon, issued from it again at Finsbury Park, after a transit of $18\frac{3}{4}$ miles, containing 0.157 part, practically an undiminished quantity of organic carbon. I have made several other similar experiments with like results. It is extremely unlikely that peaty water should be oxidised by flowing through 6,820 yards of open conduit, and should entirely refuse to combine with oxygen when it is exposed to light and at the same time most violently shaken up with air for $10\frac{1}{2}$ hours on the connecting rod of a horizontal steam engine making 100 strokes per minute (see p. 511).

I now come to Dr. Tidy's laboratory experiments on oxidation. He believes, apparently, that there is some occult influence exerted upon *running* water which is absent in the case of falling water (unless it falls naturally in a river bed, and then the influence is very strong), in the case of water dashed into foam in a glass vessel, in the case of water violently stirred up with glass rods, and especially in the case of water "exposed to light and air in a bottle." In short, this mysterious influence which so favours the oxidation of polluted water

running in rivers with numerous unpolluted affluents, appears always absent when the water is put under conditions admitting of the application of accurate experimental tests. The author has therefore had constructed a series of V-shaped troughs, lined with glass, and inclined alternately in opposite directions, so as to give a continuous flow of water through 20 troughs of the aggregate length of 200 feet. Through them he pumped six gallons of sewage water until it had performed a journey of one mile in about eight hours, and in order that the oxidising demon might not consider this arrangement too artificial, it was set out in the open "air polluted with dust and soot," and freely exposed alternately to rain and storm and "blacks;" and here at last, after many failures, the apparatus is described as working successfully, but only *at last*, for the author says, "At first I am bound to acknowledge *all my results showed absolutely against my views of oxidation.*"

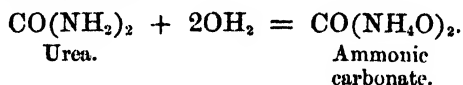
In the successful experiments the organic carbon and nitrogen in the polluted water were diminished, in some cases as much as 50 per cent., during transit through these troughs.

Now, in the first place, I submit that the running of water through this apparatus presents scarcely the remotest analogy to the flow of a river. In the V-shaped troughs the water was exposed to an enormously greater solid surface, in relation to its volume, than it would be in any river, for not only is the sectional area of the slender stream running at the angle of the gutter excessively small in comparison with the area of the containing walls, but the water spreading out upwards in thin films on the sides of the troughs would be brought into contact with an enormous surface of glass, and would be placed under conditions never occurring in a river, but which would obviously favour oxidation by contact with extensive surfaces.

Secondly, we are not informed whether the sewage was filtered before being used. If it was not, then most of the suspended organic matter would stick to the glass troughs, and a reduction of organic elements must of course follow.

Thirdly, the chief cause, however, of the diminution of organic carbon and nitrogen observed in these experiments is, in my opinion, the decomposition of the urea of the sewage into ammoniac carbonate. I have found in numerous experiments that this change is effected by bacteria, which multiply and flourish in urine so long as urea is present, but immediately die, or at least become motionless, as soon as the last traces of urea have disappeared. Urine mixed with a large volume of fresh water, and kept in clean vessels, undergoes change with extreme slowness, but when the mixture is put into vessels which have previously contained stale urine, the change of urea into carbonate of ammonia is comparatively rapid. Now sewage

contains abundance of bacterial germs, and the angles of the V-shaped troughs would present a favourable nidus for their arrest and development. Hence the failure of the experiments *at first*, and their success *at last*, for if the troughs were clean, or if anything occurred to disturb bacterial life, the sewage would pass through unchanged, but a marked diminution of organic carbon and nitrogen would ensue when the accumulation of bacteria and their germs in the troughs provided the necessary means of rapidly transforming urea into carbonate of ammonia—a transformation which is effected by the mere assimilation of 2 mols. of water by 1 mol. of urea, and which, therefore, has nothing to do with oxidation.



I have now reviewed all the quantitative experiments upon which Dr. Tidy bases his conclusion that more than 38 per cent. of the organic matter in peaty water can be got rid of by oxidation during a flow of only one mile, although, as he says, “the oxidation of *vegetable* matters is *infinitely less rapid* than the oxidation of *animal* matters.” And as these quantitative investigations fail entirely, in my opinion, to justify his conclusion, I need not enter into detail respecting the proofs of oxidation by what he calls “the naked eye inspection of rivers.” I agree in the main with his description of the phenomena observed when putrescent sewage mixes with a very large volume of river water. How its black or brown colour soon disappears, owing to the oxidation of sulphide of iron; how the offensive smell next vanishes; and, lastly, how the suspended matters are deposited in the still reaches, and the river flows on clear and transparent. The process he describes is simply the cessation of putrefaction and the deposition of sediment. During putrefaction, dissolved oxygen is used up, black sulphide of iron is formed, and fish die, although they flourish in fresh sewage; but as soon as the water has again the opportunity of becoming aerated, it again supports fish life. I also agree with the author that the growth of the sewer fungus is an absolute indication of the presence of sewage in a water, but I entirely demur to his inference that the absence of the sewer fungus proclaims the absence of sewage. My experience is that this fungus can grow only in water very highly charged with sewage, and I would remind Dr. Tidy that, in our recent inspections of the lower Thames, we saw no sewer fungus in the river, even near to the Metropolitan sewer outfalls.

The author's instances of “naked eye inspection” will not stand the test of more thorough investigation. The Soar at Leicester, after receiving the limed sewage of the town, mingles with the overflow of

clean water from a canal, and receives the Wreak and two other important and unpolluted tributaries on its way to Loughborough, where Dr. Tidy found its appearance so much improved. When the polluted water of the Skerne mingles with the much larger volume of the unpolluted Tees, putrescence ceases, suspended matters are deposited, and a naked eye inspection fails to discover the coarser evidences of sewage. Of another river the author says, "I have seen the River Irwell at Manchester polluted with every form of filth, personal and manufacturing. At Warrington, after a flow of nine miles, the offensive character of the stream had entirely disappeared." Here the "naked eye inspection" is again at fault. The Irwell flows not nine, but twenty-six miles, from Manchester to Warrington. It is no longer the Irwell, but the Mersey, when it reaches Warrington, and although the mere change of name would not affect the quality of its water, the fact that it joins the much less polluted Mersey fifteen miles above Warrington is an important one; and it was also perhaps hardly fair to omit all notice of the Bollin and seven other tributaries which join the Mersey after its union with the Irwell and before it reaches Warrington. In this case, however, there is quantitative evidence to check naked eye inspection of the quality of the water. On May 26th, 1868, I took a sample of the Mersey water as it fell over the mill weir just above Warrington, and in the following table I have contrasted the proportion of organic elements and suspended matters in this sample with those formed in the Irwell just below Manchester and in the Mersey just before its junction with the Irwell.

Date.	Description.	In solution.		In suspension.		Total.
		Organic carbon.	Organic nitrogen.	Mineral.	Organic.	
June 17, 1868	The Irwell at Throstle-nest weir	1·173	0·332	2·71	2·71	5·42
May 13, 1869	The Irwell at Throstle-ness weir	2·156	0·238	1·18	1·86	3·04
Mar. 12, 1869	The Mersey at its junction with the Irwell	0·570	0·078	0·84	0·26	1·10
May 26, 1868	The Mersey just above Warrington	1·026	0·224	1·34	0·06	1·40

Unfortunately these samples were not collected contemporaneously, and are therefore not strictly comparable, but they show that the Mersey, notwithstanding a flow of 15 miles after its junction with the Irwell, arrives at Warrington in a badly polluted state, and further, that in the face of the foregoing analyses, there is no occasion to call

in the aid of infinitely rapid oxidation to account for the reduction of organic elements in the Irwell from 1.505 or even 2.394 parts per 100,000 to 1.250 part in the combined Mersey and Irwell, when the Mersey itself, before junction, contains only half as much as the combined streams, or 0.648 part per 100,000.

If, then, there is no evidence whatever of the destruction by oxidation of the dead organic matter of sewage by a flow of a dozen miles or so in a river, still less is there any ground for the assumption that the organised and living matter of sewage is so oxidised, or even otherwise destroyed, under like circumstances. I leave to biologists and others who have specially studied the habits and development of microscopic organisms, Dr. Tidy's suggestion that disease germs when poured along with sewage into a river "very soon suffer complete destruction by the bursting of their envelopes owing to the powerful endosmic action of the water in which they are immersed;" but as regards the rapid destruction of these germs by oxidation, I can testify that bacteria develop, multiply, and flourish for weeks in attenuated liquids, no matter whether these liquids are kept in contact with oxygen, atmospheric air, or carbonic anhydride. They appear to be perfectly indifferent to the quality of the gas dissolved in the water, so long as they find congenial molecules capable of yielding active energy by transformation into new molecules.

Relative to this branch of the subject I have received the following letter from Professor Tyndall:—

"I have glanced over Dr. Tidy's paper generally, and have read with care what he says regarding germs. It is very plausible, but, in my opinion, utterly chimerical. It would give me extreme pleasure to subject him before his peers to five minutes' cross-examination. Nothing, for example, is more clearly established than that the phenomena of ordinary putrefaction arise from the multiplication of bacteria. This is no "theory," it is a fact. Well, what about the *germs* of bacteria? Do they commit suicide by endosmic action? So far is this from being the case, that Dr. Tidy cannot take a single drop of water from his tap that does not contain living germs, capable, when placed in a proper nutritive fluid, of developing themselves into countless multitudes of bacteria. Such germs are demonstrably not killed by this hypothetical endosmic action. Pray ask Dr. Tidy what reason has he to suppose that other germs must behave differently from those of *Bacterium termo*. If germs once communicated to river water do not increase and multiply, it is simply because the conditions necessary to their nutrition are not present. I have carried my experiments on water from the sea level up to 8,000 feet above that level in the Alps, and nowhere have I found the slightest countenance given to the endosmic action, so lightly assumed by Dr. Tidy.

"I wish I had time to write more fully on a subject which interests me profoundly, because it is of such unspeakable importance to the public."*

Dr. Tidy is fond of appealing to *à priori* impressions and foregone conclusions; he asks if burning up or oxidation in running water is not exactly what might be expected; he says that "vast masses of organic *débris*, and myriads of dead epithelial scales from every membrane visible and invisible," are daily sent into the air; and asks, who doubts for a moment that they are daily burnt up, and thus prevented from acting injuriously. For myself, I do venture to doubt this dogmatic statement. Having been engaged for the greater part of my life in exposing organic matters, of the most varied composition, to air for periods which were frequently of long duration, I have not found (except in an extremely small number of cases, which, moreover, never occur in nature) that these substances are burnt up either in a day, or a month, or a year. Let Dr. Tidy put some organic *débris* or epithelial scales upon the pan of a delicate balance, and watch the diminution of weight by rapid burning up, and I venture to predict that before he notices the complete disappearance of a single scale, or any very marked diminution in the weight of the mass of *débris*, he will have grown tired of continuing the experiment. Has Dr. Tidy ever looked on the top of his book cases; and, if so, has he ever considered why the organic dust collected there has not been burnt up by the air through which it has slowly subsided, and with which it has ever since been in contact? What a saving in servants, and what an increase in cleanliness would result, if the author's dogma could be made a reality! It was, I think, Miss Nightingale who first directed attention to the vicious method of "dusting" employed by servants. She said they only flicked the dust from one part of a room to another, instead of removing it. But, according to Dr. Tidy, the servants are quite right; they *aërate* the particles of dust, and cause them to be immediately burnt up, or, to use his own words, "thereby burning them up, and preventing them from acting injuriously." Although I am not a medical officer, and may perhaps be deemed to have no right to offer such an opinion, yet I venture to think that persons unprotected from those diseases would consult their own safety by avoiding

* In the discussion which followed the reading of this paper, Professor Huxley pointed out that the epidemic diseases—splenic fever, pig typhoid, and the cholera of fowls, were invariably caused by bodies of the nature of bacteria, which could be cultivated through many generations, and then, on infection of the appropriate animals, give rise to the characteristic disease. He said there was every reason to believe that analogous diseases in man were caused by similar organisms. As to the bursting of the envelopes of germs in water, it was a question whether they had any envelopes. Ordinary water was full of bacteria germs, and there was no reason to suppose that either oxidation or endosmosis would affect them.

the breathing of air which had a few hours previously "been polluted by the scales of a person suffering from scarlet fever, or the infected breath of a measly patient."

For the same reason, I also think that it would be for the benefit of the public health that communities should not be supplied, for dietetic purposes, with river water which, *as river water*, has been mixed with sewage. And I confidently endorse to-day the opinion expressed six years ago by the Rivers Pollution Commissioners, that the supply of unpolluted deep-well water, like that of the Kent and Colne Valley Companies, would be a priceless boon to the Metropolis, "and would at once confer upon it absolute immunity from *epidemics* of cholera." This opinion is founded upon the following facts:—

1. On the authority of the late Sir William Lawrence, F.R.S., Bethlem Hospital and the "House of Occupations," containing 700 persons, were supplied with water from a deep well sunk upon the premises in 1825. Sir William says, "there was not a single case of cholera in the hospital or House of Occupations during the severe epidemics of 1832, 1849, or 1854, although the immediately surrounding neighbourhood suffered severely, especially in the two later visitations. Before the last cholera epidemic in 1866, the inmates of Bethlem Hospital had been removed."

2. On the authority of Surgeon-Major A. C. C. De Renzy, now Sanitary Commissioner in India, the inmates of Millbank Prison suffered severely from cholera in the epidemics of 1832 and 1849, whilst they were supplied with Thames water. In the next cholera epidemic of 1854, the prisoners were again attacked, but the disease was at once extinguished by changing the water supply. Surgeon-Major De Renzy says, "The water supply was changed on the 10th of August, 1854. The new source of supply was the artesian well in Trafalgar Square. The change was carried into effect in the midst of the cholera epidemic which so severely visited London that year, and the prison was suffering from cholera at the time. *Six days after the change the disease suddenly stopped*, and a marked improvement took place in the health of the prison. From the date of the introduction of the new water supply up to April of the present year (1872)—a period of nearly nineteen years—there have been only three deaths from typhoid, viz., one in 1855, one in 1860, and one in 1865. Of these the last occurred in a convict who was suffering from the disease at the time of his admission. In the first part of 1854, and before the change of water supply, there had been three deaths from fever and two from diarrhœa. In the nineteen years since the change of water supply, there has been only one death from diarrhœa and dysentery." In the fourth epidemic of cholera, that of 1866, the convicts entirely escaped.

3. On the same authority, Pentonville Prison has never suffered from cholera, though three epidemics of that disease have visited London since the prison was established in 1843. During the whole of this time Pentonville Prison drew its water exclusively from a deep well in the chalk.

Dr. Tidy quotes certain comparative death statistics, compiled by Mr. Baldwin Latham, for the purpose of showing that enteric fever, scarlatina, diarrhœa, diphtheria, and dysentery are more prevalent in certain metropolitan districts supplied with the Kent Company's water, taken from deep wells in the chalk, than in certain other districts supplied with Thames water. Nothing is more fallacious than such comparisons of isolated districts selected for the purpose, unless there is conclusive evidence that the numerous other conditions affecting the salubrity of the compared districts are substantially the same, and there is no such evidence in the cases quoted. Very different is the result arrived at by the Registrar-General, in comparing the whole waterfield of the Kent Company with the aggregate fields of the companies drawing from the Thames and Lea; for, in his return for the week ending July 20th, 1878, he says:—"In London the high mortality of the week was due to diarrhœa, which always becomes fatal in London, when the temperature of the Thames water rises above 60° F. Thus the temperature of the water, which had been 60°, rose in the last week of June to 65°. In the three following weeks it was 68°, 66°, and 67°, and the weekly deaths from diarrhœa and simple cholera, which stood at 23, rose to 78, 156, 256, and 349 in the corresponding weeks. The deaths from diarrhœa were differently distributed over the areas of the water companies. Thus the deaths in the last four weeks were 786 in the districts supplied by Thames and Lea waters, whereas the deaths in the districts supplied with water drawn from the chalk by the Kent Company were only 19. Out of the same population, the deaths were as in the ratio of three to one." Again in the return for the following week, ending July 27th, 1878, he says:—"The deaths referred to diarrhœa and simple cholera, which in the five preceding weeks also rapidly increased from 23 to 349, and further rose the following week to 457, of which 336 were of infants under one year of age, and 99 of children aged between one and five years. . . . During the same period the annual death-rate from diarrhœa within the area supplied by the Kent Company from deep wells in the chalk was 1·7 per 1,000, whilst in the other parts of the metropolis supplied with water from the rivers Thames and Lea, the diarrhœa death-rate averaged 3·7 per 1,000."

In conclusion, I cordially agree with Dr. Tidy, when he says of water supplied to a community:—"Given an impure source, there is no help that I can see but the entire abandonment of the source. Art

may be fairly asked to improve a good water, but *it is simple madness to ask her to deal with bad water.*" And again—"that impure water has been one of the most active causes of disease is a fact which, to my mind, has been proved beyond doubt. The researches of Dr. Ballard at Islington on typhoid, caused by the admixture of polluted water with milk, the Caterham outbreak, the numerous cases of disease resulting from drinking impure surface well water, supply evidence that should make us very jealous indeed of allowing a water to be used for drinking over which hangs *the merest shadow of a suspicion.* No one can be too strictly a water purist." I will only seek to enforce these clear and unmistakable expressions of Dr. Tidy's opinion by adding to the instances he quotes, the cases of London, Manchester, and Glasgow, in which tens of thousands of people have fallen victims to cholera, owing to the supply of polluted river water.

I submit, therefore, that the question asked at the commencement of this paper—"Can running water be at all times safely used for dietetic purposes a few hours or days after it has been mixed with sewage?" must be answered in the negative.

XLII.—On some Products of the Oxidation of Paratoluidine.

By W. H. PERKIN, F.R.S.

In a paper on mauveine and allied colouring matters, published in the Journal of this Society last year, I referred to some experiments on the oxidation of paratoluidine by chromic acid (*Journ. Chem. Soc.*, 1879, 728). Since then the subject has been further studied, and I now beg to lay before the Society the results which have been obtained.

For the oxidation of the paratoluidine a solution of its sulphate was mixed with a solution of potassic dichromate, molecular proportions of the substances being used. On standing for about 24 hours, a large quantity of a brown precipitate formed. This was collected, washed, dried, and exhausted with benzene, which became coloured a rich orange-red. The extract thus obtained was filtered, and concentrated to a small bulk by distilling off most of the benzene, and after standing for some time deposited a quantity of a red crystalline product. This was collected and pressed between bibulous paper. It generally amounted to about 10 per cent. of the paratoluidine used. It was then crystallised from alcohol, in which, however, it is diffi-

cultly soluble. The analyses of the first preparations of this substance gave numbers agreeing with the formula C_7H_7N , but products subsequently obtained, although having exactly the same appearance, gave variable numbers on combustion. Purification by crystallisation from ether was then tried, but still no definite results were obtained. It was afterwards noticed that the greatest differences in the percentages of carbon and hydrogen existed between the first and last crops of crystals, thus indicating that more than one substance was present. In fact it was found to consist of two products very similar in appearance.

After a time the least soluble of these was obtained in a pure state by repeated crystallisations from ether. Various specimens were subjected to analysis, and gave the following numbers. It is a difficult substance to burn. It was dried at 100° .

I.	0.2588 gram of substance gave
	0.1573 „ of OH_2 and
	0.7601 „ of CO_2 .
II.	0.2583 „ of substance gave
	0.1624 „ of OH_2 and
	0.7590 „ of CO_2 .
III.	0.1938 „ of substance gave
	0.1176 „ of OH_2 and
	0.5659 „ of CO_2 .
IV.	0.1260 „ of substance gave
	0.0761 „ of OH_2 and
	0.3698 „ of CO_2 .
V.	0.1810 „ of substance gave
	0.1082 „ of OH_2 and
	0.5304 „ of CO_2 .
VI.	0.2168 „ of substance gave
	23.5 c.c. of N at 10.4° C. and 765 mm.
VII.	0.1876 gram of substance gave
	20.875 c.c. of N at 11.4° C. and 756.5 mm.

These numbers give percentages which agree with the formula— C_7H_7N .

	Theory.	Experiment.			
		I.	II.	III.	IV.
Carbon	80.00	80.10	80.13	79.69	80.06
Hydrogen ..	6.66	6.78	6.98	6.74	6.54
Nitrogen	13.34	—	—	—	—

	Experiment.		
	V.	VI.	VII.
Carbon	79.61	—	—
Hydrogen	6.64	—	—
Nitrogen	—	13.06	13.14

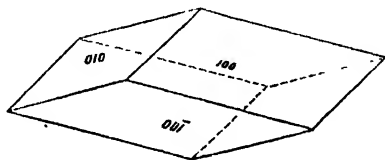
For reasons to be explained further on, this formula requires to be multiplied by 3, which makes it $C_{21}H_{21}N_3$.

I propose provisionally to call it *triparatolylene triamine*.

This substance when heated melts at about $216-220^\circ$, with decomposition, and then dissolves in alcohol acidified with acetic acid, with a brown colour. It is moderately soluble in benzene, not quite so much so in ether. From these solvents it separates out in beautiful garnet-red crystals. It also crystallises easily from chloroform, but does not give such well-defined crystals. It is very slightly soluble in cold alcohol, and but little so when boiling. The same is true of petroleum spirit, but the solubility is even less in this case. When crushed it forms an orange-vermilion powder. Mr. Fletcher has measured some of the crystals deposited from ether and from benzene, and has kindly sent to me the following report:—

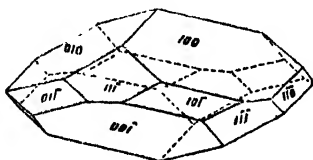
“The crystals are of an evident rhombohedral habit, most of them presenting the form of a somewhat obtuse rhombohedron. Examination with the help of the goniometer confirmed the conclusions deduced from mere inspection. The faces are often striated and give multiple reflections, more especially in the case of those crystals which have been obtained by deposition from ether. The aspect of the rhombohedron (100) is given by Fig. 1. In many instances the lateral

Fig. 1.



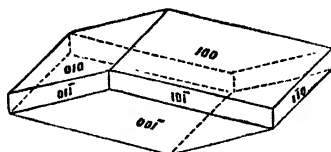
edges of this rhombohedron are truncated by the faces of the prism $(10\bar{1})$, as shown in Fig. 2. On some of the crystals obtained by depo-

Fig. 2.



sition from benzene a second rhombohedron ($\bar{1}11$) is present, as shown in Fig 3. The faces of this latter rhombohedron are always rounded,

Fig. 3.



and when observed in the goniometer telescope give a long band of faint images, terminating in a bright and distinct one.

"The calculated angle ($100 \cdot 111$) is $29^\circ 9'$.

"The following measured angles were obtained from different edges of a crystal deposited from benzene:—

Angle.	Calculated.	Observed.					
$100 \cdot 010$	$49^\circ 54'$	$49^\circ 53'$	$49^\circ 54'$	$49^\circ 54'$	$49^\circ 38'$	$49^\circ 27'$	
$100 \cdot 1\bar{1}1$	40 9	39 58	39 46	40 20	40 26		
$1\bar{1}1 \cdot 0\bar{1}1$	49 51	49 58	49 31	50 16			
		49 54	49 25	49 1			
$100 \cdot 1\bar{1}0$	65 3	64 48	65 22	65 18	65 1	64 56	
		65 21	64 42	64 45	65 38		
$100 \cdot \bar{1}11$	77 16	77 16.					

"To confirm the conclusion arrived at with regard to the system of crystallisation, a section was made perpendicular to the line joining the obtuse angles of one of the rhombs, and examined with convergent plane polarised light. The usual circular rings with two rectangular brushes, characteristic of a uniaxial crystal, were obtained. By the help of a quarter undulation plate it was shown that rays of light travel more quickly along the crystallographic axis than perpendicularly with respect to it, and thus the crystal is positively uniaxial."

Triparatolylene triamine is an organic base, but its salts soon undergo complete change.

It dissolves easily in alcohol acidified with a small quantity of hydrochloric acid, forming a clear brownish-red solution. This on standing for even an hour or less changes in colour to a red-purple, and if heat be employed the change is very rapid. If the solution be then rendered alkaline it forms a yellowish-scarlet solution, which when diluted deposits a chocolate-brown powder, consisting of a new base, forming a purple hydrochlorate.

Triparatolylene triamine dissolves in concentrated sulphuric acid

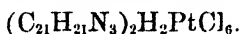
with a magnificent clear blue colour. This changes to a very pale purple on dilution. Its hydrochloric solution is rapidly decolorised if granulated tin be added to it. Boiled with aniline and a little acetic acid it becomes brown.

None of the above coloured solutions, so far as they have been examined with the spectroscope, give absorption bands, though they give strong general absorptions.

Being desirous of obtaining some knowledge of the molecular weight of triparatolylene triamines, and as the ordinary salts were too unstable to give any information on this subject, I made experiments upon the preparation of a platinum salt. For this purpose a quantity of the base was dissolved as rapidly as possible in cold alcohol, acidified with hydrochloric acid. The solution was filtered and mixed with alcoholic platonic chloride; this did not give any precipitate. Water was then added in excess, which caused a purplish chocolate precipitate to form. This was collected on a vacuum filter, rapidly washed, and then dried in a vacuum. The preparation of this salt was usually made in less than half an hour. Two preparations were analysed and gave the following numbers. They were dried in a vacuum.

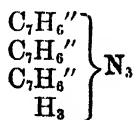
I.	0.2157	gram of substance gave
	0.0876	„ of OH ₂ and
	0.3808	„ of CO ₂ .
II.	0.1594	„ of substance gave
	0.0295	„ of Pt.
III.	0.2341	„ of substance gave
	0.0440	„ of Pt.

These numbers give percentages agreeing with the formula -



		Experiment.		
	Theory	I.	II.	III.
Carbon	48.35	48.14	—	—
Hydrogen	4.22	4.51	—	—
Platinum	18.80	—	18.52	18.78

It is principally owing to these results that I give the formula $\text{C}_{21}\text{H}_{21}\text{N}_3$ to triparatolylene-triamine. Its constitution may be represented thus—



but most likely is not of such simple constitution. It is also not improbable that it may be in some way or other related to mauveine,

because when preparing that colouring matter by oxidising a mixture of paratoluidine and aniline, it does not seem to be formed, or at any rate not to the same extent as when aniline is not present, and it differs from mauveine by C_6H_3N .

$C_{27}H_{24}N_4$ mauveine

$C_{21}H_{21}N_3$ triparatolyene triamine

C_6H_3N

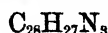
The second and more soluble product already referred to, was contained in the ethereal mother-liquors from the preparation of triparatolyene triamine. Considerable difficulty was experienced in obtaining this in a pure state. The process adopted was one of fractional crystallisation, first by concentrating the mother-liquor little by little and removing the crops of crystals as they separated until most of the triparatolyene triamine had separated out, and then after distilling off all the ether, fractionally crystallising the residue by dissolving out the most soluble part with a limited amount of ether, and concentrating, the process being repeated until the body was found to be pure. In some preparations the purification was accomplished by crystallisation from petroleum spirit (b. p. 70—100°) instead of ether. The purity of the product can be ascertained by dissolving a small quantity in cold concentrated sulphuric acid, with which it forms a dull violet solution, changing to a yellowish-green. Should triparatolyene diamine be present it will be seen to form light blue streaks in the solution.

The following numbers were obtained on the analysis of various preparations dried at 100° C. :—

I.	0.2371	gram of substance gave
	0.7207	„ of CO_2 .
II.	0.1572	„ of substance gave
	0.0955	„ of OH_2 and
	0.4795	„ of CO_2 .
III.	0.1282	„ of substance gave
	0.0831	„ of OH_2 and
	0.3891	„ of CO_2 .
IV.	0.1422	„ of substance gave
	0.0872	„ of OH_2 and
	0.4315	„ of CO_2 .
V.	0.1103	„ of substance gave
	0.0678	„ of OH_2 and
	0.3342	„ of CO_2 .

- VI. 0.1196 gram of substance gave
 0.0747 „ of OH_2 and
 0.3628 „ of CO_2 .
- VII. 0.2114 „ of substance gave
 18.75 c.c. of N at 10.5°C . and 756.5 mm.

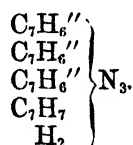
These numbers give percentages leading to the formula—



		Experiment.			
	Theory.	I.	II.	III.	IV.
Carbon	82.96	82.92	83.18	82.77	82.81
Hydrogen ..	6.67	—	6.74	7.2	6.82
Nitrogen....	10.37	—	—	—	—

		Experiment.		
		V.	VI.	VII.
Carbon		82.63	82.72	—
Hydrogen		6.83	6.9	—
Nitrogen		—	—	10.55

It may be viewed as triparatolylene triamine with one atom of hydrogen replaced by tolyl, thus—



I therefore propose to call it *tolyltriparatolylene triamine*.

This substance melts at about 175°C . with decomposition. It then dissolves in alcohol acidified with acetic acid, with a purple colour.

It is moderately soluble in ether, from which it separates in small flat prismatic crystals. It is less soluble in petroleum spirit, but crystallises out from this solvent on standing in larger crystals than from ether. They appear as transparent scales of a rich brown-red colour by reflected light, and dark red by transmitted light. When viewed with a lens they are seen to be tabular oblique prisms, not unlike potassic chlorate in form. Benzene dissolves this substance easily, but deposits it only in very small crystals. I am inclined to think it forms an unstable compound with this substance.

Tolyltriparatolylene triamine is an organic base, forming rapidly decomposable salts. It dissolves easily in alcohol acidified with hydrochloric acid, yielding a dull purple-coloured solution of the hydrochloride. This undergoes a complete change after a time, the colour becoming indigo-blue. It then contains a new base. In concentrated

sulphuric acid it dissolves with a dull violet colour, quickly changing to a pale yellowish-green. This solution on being diluted with water becomes nearly colourless.

A platinum salt was prepared in exactly the same manner as that of triparatolylene triamine. It is a purple-brown powder, and on analysis gave the following numbers:—

0.1184 gram of substance gave
0.0191 „ of platinum = 16.13 per cent.

The formula $(C_{28}H_{27}N_3)_2H_2PtCl_6$ requires 16.15 per cent.

In the preparation of the foregoing products by means of sulphate of paratoluidine and potassic dichromate a large quantity of a brown powder containing chromium is always formed, therefore experiments were made with a view of obtaining a better process and avoiding the formation of this brown product. It has been observed that if acetic acid be employed instead of sulphuric acid in oxidation processes of this nature that the chromium remains in solution. A solution of paratoluidine in ordinary 50 per cent. acetic acid was therefore taken and mixed with the usual quantity of potassic dichromate in aqueous solution and allowed to stand for about 24 hours. The somewhat soft resinous product which formed was washed with water and then with cold alcohol; this gradually dissolved most of the products, leaving a bright-red crystalline powder consisting of the substance required; the amount, however, was not greater than that obtained by the original process, and it did not appear to possess any special advantages over it.

By slightly modifying this process a remarkable difference in the product formed was observed. This modification consisted in treating a solution of paratoluidine in glacial acetic acid with a solution of chromic acid in the same solvent, the quantity used being about equivalent to the potassic dichromate used in the previous experiments. In this case the mixture soon commenced to deposit a quantity of beautiful golden-yellow needles. These when purified proved to be parazotoluene, and gave the following numbers on analysis:—

0.2019 gram of substance gave
0.1297 „ of OH_2 and
0.5893 „ of CO_2 .

	Theory for $C_{14}H_{14}N_2$.	Experiment.
Carbon	80.0	79.69
Hydrogen.....	6.6	7.1

The fusing point, however, was found to be higher than that given by the discoverers of this body. It was 143° , that given being 137° . On account of this discrepancy it was thought desirable to prepare

some from pure paranitrotoluene. The operation was conducted as follows:—A solution of about 20 grams of pure paranitrotoluene in alcohol was agitated with a quantity of sodium amalgam which was added at various intervals. The reaction was energetic, and the mixture had frequently to be cooled down. After a time a brown product commenced to separate and eventually increased so as to render the fluid quite thick; when the reaction was over and the product cold the mercury was separated and the solid product collected in a filter and washed with alcohol; it was then washed with water to remove alkaline products, dried, and boiled with glacial acetic acid, in which it mostly dissolved. The filtered solution on cooling deposited a mass of yellow needles of parazotoluene. To purify this further it was distilled and again crystallised. Thus obtained, it fused at 142—143°.

While making these experiments it was thought desirable to repeat them, using orthonitrotoluene instead of the para; in this case however, but very little orthazotoluene was obtained, and it is believed that even this resulted from the action of the sodic hydrate formed and not from the sodium amalgam. In confirmation of this I may refer to an experiment on the action of caustic alkali on orthonitrotoluene. A quantity of this body was treated with alcoholic potassic hydrate and distilled; at first a basic oil, most probably orthotoluidine, came over and then a red oil. On treating this with hydrochloric acid to remove basic products, a considerable quantity of a red easily fusible crystalline mass of crude orthazotoluene was obtained.

Curiously, paranitrotoluene behaves very differently when treated with an alcoholic solution of potassic hydrate. After boiling a short time a thick crystalline paste separates, and this, when washed with water and dried, is insoluble or nearly so in solvents, and cannot be distilled without complete decomposition.

XLIII.—On Dibromanthraquinones and the Colouring Matters derived from them.

By W. H. PERKIN, F.R.S.

GRAEBE and LIEBERMANN describe two processes for the preparation of dibromanthraquinone; one of these consists in brominating anthraquinone, the other in oxidising tetrabromanthracene (*Ann. Chem. Pharm.*, Sup. vii, 288—289; *Moniteur Scientifique*, April, 1879, 397—398). As nothing is said to the contrary, it would appear that these processes yield the same body. As I have had occasion to prepare

dibromanthraquinone I have employed both methods, but find they give isomeric and not identical products. In the following account of these bodies I shall designate them as α and β .

α -Dibromanthraquinone.

This product was prepared by brominating anthraquinone and afterwards purifying it by crystallisation from benzene (or better, high boiling naphtha), as described by Graebe and Liebermann. I have found it an improvement, however, to distil the crude product before distillation. On analysis it gave the following numbers:—

0.1076 gram of substance gave
 0.1812 „ of CO_2 and
 0.0179 „ of OH_2 .

	Theory for $\text{C}_{14}\text{H}_6\text{Br}_2\text{O}_2$.	Experiment.
Carbon	45.90	45.91
Hydrogen	1.63	1.84

α -Dibromanthraquinone fuses at 145°C ., and when more strongly heated distils with but little decomposition. It is very slightly soluble in boiling alcohol, but rather more so in boiling glacial acetic acid. In boiling coal-tar naphtha it is moderately soluble, but on cooling is rapidly deposited in small plates, and these when pressed between bibulous paper have a satiny aspect. It dissolves in concentrated sulphuric acid with an orange-yellow colour, and on the addition of water is precipitated.

β -Dibromanthraquinone.

This was prepared by oxidising tetrabromanthracene. For this purpose a solution of chromic acid in glacial acetic acid was employed. It was found best to employ a large excess of glacial acetic acid, owing to the insolubility of the tetrabromanthracene, and to continue the boiling of the mixture for a long time, otherwise much unchanged product remained; small operations were also found to work better than large ones, owing to the violent bumpings which take place if any considerable quantity of material is used. The oxidised product was collected, washed, dried, and repeatedly crystallised from high boiling naphtha, until its fusing point was about 275°C . Thus prepared, it gave the following numbers:—

0.1022 gram of substance gave
 0.1714 „ of CO_2 and
 0.0170 „ of OH_2 .

These numbers give percentages closely agreeing with those required by theory, viz.:—

Carbon	45.72
Hydrogen	1.84

β -Dibromanthraquinone fuses about 30° higher than its isomeride, viz., at 174 — 175° C.; with solvents it behaves in a similar manner to the α body, except that it is rather less soluble. It crystallises in needles, similar to anthraquinone. It can be distilled with but little decomposition.

Decomposition of α - and β -Dibromanthraquinones with Caustic Alkali.

It has been stated that dibromanthraquinone, prepared by either of the above processes, yields alizarin when fused with alkali; seeing that the bodies thus produced are isomeric, this appeared very remarkable. Experiments were therefore made in this direction, and first with α -dibromanthraquinone, as it would appear from Graebe and Liebermann's paper already referred to, that the colouring matter they submitted to analysis was prepared from β -dibromanthraquinone, and not from the α body.

For the fusion of the α - and also the β -dibromanthraquinone with potassic hydrate, I found the most convenient arrangement to consist of a platinum dish, the bottom of which dipped into spermaceti heated to about 250° C. (Graebe and Liebermann employed 250 — 270°). About 10 grams of alkali was used in an operation, and into this when fused about 1 gram of the dibromanthraquinone was stirred, having been previously ground into a paste with a saturated solution of potassic hydrate. After a few moments the mixture began to get blue at the edges, and then soon became a black mass; this was stirred, but only occasionally, as it was thought that constant stirring caused oxidation to take place. The mixture was heated for about twenty minutes: on the addition of water the product dissolved, forming a blue-violet solution.

A number of these operations were made, and the solutions of the combined products filtered from unchanged α -dibromanthraquinone. This solution when viewed with the spectroscope, gave the alizarin bands, but they appeared hazy. The colouring matter was precipitated by means of hydrochloric acid, washed, dried, and boiled with alcohol; on standing colouring matter crystallised out. This was collected and recrystallised twice. On analysis it gave the following numbers:—

0.0908	gram of substance gave
0.2330	„ of CO_2 and
0.0298	„ of OH_2 .

	Theory for $C_{14}H_8O_4$.	Experiment.
Carbon	70.0	69.98
Hydrogen	3.33	3.64

This substance was therefore a dioxyanthraquinone, and its properties as a dye, its absorption spectrum, and behaviour with reagents, was evidently alizarin.

- On concentrating the mother-liquors from which this alizarin had been obtained, a second crop of crystals separated; these evidently contained a good deal of alizarin, but patterns dyed with them gave brighter reds than alizarin does. It was therefore dissolved and boiled with baryta-water; with this it formed a violet precipitate of baric alizarate and a purple solution. This was filtered off, and the residue boiled with fresh quantities of water until it ceased to be coloured.

The purple solution was boiled, acidified, and allowed to stand until cold. The colouring matter which had deposited was then collected, washed, dried, and crystallised from alcohol, and the resulting crystals analysed. Unfortunately I did not have sufficient product to allow me to crystallise a second time, therefore it was not absolutely pure, but nevertheless gave the following numbers, which are sufficiently good to show its composition:—

0.0961 gram of substance gave
 0.2327 „ of CO_2 and
 0.0300 „ of OH_2 .

	The formula $C_{14}H_8O_4$ requires	Experiment.
Carbon	65.62	66.02
Hydrogen	3.12	3.46

There can be no doubt that this substance was anthrapurpurin, as it gave the characteristic reds, blacks, and purples with mordants, and also possessed the other properties of this body.

The original mother-liquor from which the crop of alizarin and anthrapurpurin had been obtained, was then boiled with baryta-water, in this case a violet precipitate and purple solution was obtained; this latter, however, was redder and browner than that from which anthrapurpurin had been obtained. The colouring matter obtained from the solution dissolved in ammonia with a reddish-brown purple colour, and behaved like a mixture of flavopurpurin and anthrapurpurin;* this was also seen in the patterns of mordanted cloth dyed with

* By the use of a solution of baric hydrate, Auerbach obtained from artificial alizarin a product which he called "Isopurpurin" (*Moniteur Scientifique*, August 1872, 686). He has also stated that it is identical with anthrapurpurin ("Auerbach on Anthracene," translated by Crookes, 203), and, unfortunately I, amongst

it, and there can be no doubt that this was the nature of the product. Unfortunately the small amount I had at my disposal prevented me separating the flavopurpurin in a pure state.

The violet baric precipitate obtained in this last operation was decomposed with hydrochloric acid, and the colouring matter examined. It was found to consist chiefly of alizarin; part of it, however, was very soluble in ether, and I was induced to regard it as a secondary colouring matter, but on further examination I believe it to be alizarin mixed with some resinous matter which causes it to dissolve more freely in ether than it otherwise would, and at the same time interferes with its solubility in water, and hence its dyeing powers.

A quantity of β -dibromanthraquinone was then fused with caustic alkali in the same manner as the α -isomer. The blue-violet solution in this case gave the alizarin bands quite sharply when viewed with the spectroscope. The colouring matter was precipitated by an acid, washed, dried, and crystallised from alcohol. It gave the following numbers on analysis:—

I.	0.1247 gram of substance gave
	0.3213 „ of CO ₂ and
	0.0371 „ of OH ₂ .
II.	0.0976 „ of substance gave
	0.2514 „ of CO ₂ and
	0.0300 „ of OH ₂ .

		Experiment.	
		I.	II.
Carbon 70.00	70.2	70.26
Hydrogen 3.33	3.3	3.42

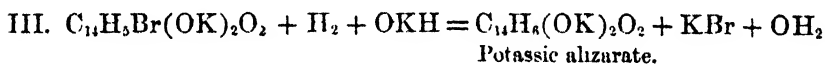
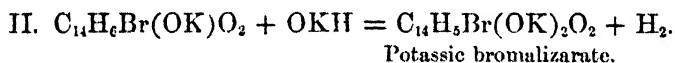
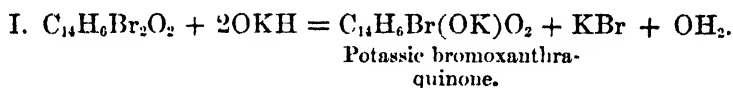
This substance was therefore alizarin, and appeared to be practically the only colouring matter produced in the decomposition of β -dibromanthraquinone by alkali. From this I am inclined to believe that the bromine in this body occupies the same position as the hydroxyls in alizarin.

The formation of alizarin from the α -dibromanthraquinone is very others, have quoted this statement (Lecture on the History of Alizarin, &c., *Jour. Soc. Arts*, May 30, 1879). My attention having been drawn to it as inaccurate, I have referred to Auerbach's original paper already referred to, and from the description he gave of his product, it evidently was not a definite body, but a mixture of flavopurpurin and anthrapurpurin: moreover, as it is said that it dissolved in ammonia with a brownish-red colour, and produced on mordanted cloth violet of a brownish shade, it probably contained more of the former than of the latter colouring matter.

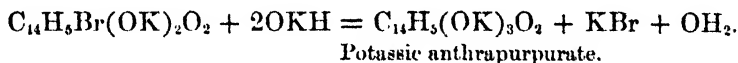
remarkable, and the only explanation of the reaction which has occurred to me is the following :—

As α -dibromanthraquinone when fused with alkali not only yields alizarin but also considerable quantities of anthrapurpurin, it is very probable that the two atoms of bromine occupy the same positions as the HSO_3 groups in β -disulphoanthraquinonic acid. If this be so we may assume that these two bromine atoms, being in separate benzene nuclei, are not attacked with equal readiness with fused potassic hydrate; the effect of this would be that the first product of the reaction would be the replacement of one atom of bromine by hydroxyl, and consequently the formation of a bromoxanthraquinone.

In the second stage this would probably undergo oxidation just as monoxanthraquinone does when heated with alkali, and thus a brom-alizarin would be formed, but as nascent hydrogen is formed during this oxidation process, this would immediately attack the bromine and replace it, and thus alizarin would be formed. These changes may be expressed thus :—



The formation of anthrapurpurin is easily accounted for if we assume that a portion of the potassic bromalizarate formed escapes the action of the nascent hydrogen, and is decomposed by the alkali thus :—



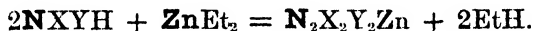
The flavopurpurin found associated with the alizarin and anthrapurpurin in this reaction is present in only very small quantities, and apparently must result from some molecular change.

XLIV.—On the Action of Organo Zinc Compounds upon Nitriles and their Analogues.

By E. FRANKLAND, F.R.S.

IN the year 1857 (*Proc. Roy. Soc.*, **8**, 502), I communicated to the Royal Society the results of an investigation into the action of zinc ethyl upon ammonia and its analogues, showing that an atom of hydrogen (in direct combination with nitrogen) was removed from each molecule of the nitrogenous body, and became replaced by a zinc bond. Thus from ammonia and zinc ethyl, zinc amine was found $\text{Zn}(\text{NH}_2)_2$.

The reaction was followed out with aniline, diethylamine, oxamide, and acetamide, and its general nature is expressed by the following equation:—



In this equation X and Y may be either hydrogen or monad positive radicals. It will be observed that in all the substances operated upon there was at least one atom of hydrogen directly combined with nitrogen, and that this hydrogen was the point of attack for the zinc ethyl. I promised, however, to extend the reaction to nitrile bases, and I propose now in conjunction with some of my pupils to redeem this promise by investigating the action of zinc ethyl and its analogues upon such nitrogenous bodies as do not contain hydrogen in this form of combination. The following examples are a first instalment of the work:—

1. Action of Zinc Ethyl on Azobenzene.

By E. FRANKLAND, F.R.S., and D. A. LOUIS, Esq.

When azobenzene is added to an ethereal solution of zinc ethyl, and the mixture is warmed to the boiling point of the ether, a reaction commences, accompanied by evolution of a large volume of gas. If an ethereal solution of the proper concentration has been employed, the action continues without further heating. As soon as it ceases, a fresh quantity of azobenzene must be added, heating as before, in order to start the reaction. This process is repeated until the reaction becomes sluggish, care being taken to employ an excess of zinc ethyl. A too sudden addition of azobenzene, or a too great concentration of the solution of zinc ethyl is to be avoided, since under these circumstances the reaction is apt to take place with explosive violence. Finally, the product is heated on the water-bath, until all the ether has been driven off, and no further gas is evolved.

In our experiments, the resulting substance was an amber-coloured jelly, which, when cold, was almost solid. It was decomposed by the addition of water, a large volume of gas being evolved. At the same time, a reddish-brown oil separated out among the zincic hydrate. On treating a portion with excess of hydrochloric acid, the oil went into solution along with the zincic hydrate. On the other hand, it was found that an excess of caustic soda dissolved the zincic hydrate, leaving the oil floating on the surface. The entire quantity was therefore treated in this way, and the oil was separated from the aqueous solution, which was further shaken with ether, to extract an additional quantity of the oily body. The oil was a base, and formed crystallisable salts. The addition of dilute sulphuric acid to an alcoholic solution of an excess of the oil produced a white crystalline precipitate, which dissolved in hot alcohol, and crystallised, to all appearance pure, in white shining leaflets. Two sulphuric acid determinations yielded the following results:—

- I. 0.1284 gram gave 0.1043 gram baric sulphate.
 II. 0.2718 gram gave 0.2230 gram baric sulphate.

	Calculated for aniline sulphate, $\text{SO}_2(\text{NPhH}_2\text{O})_2$. In 100 parts.	Found.	
		I.	II.
S	11.26	11.15	11.26

As these numbers seemed to point to aniline, the base was distilled. The entire liquid, with the exception of a small portion boiling above the range of the thermometer, came over between 180° and 190° . After fractioning two or three times, the greater portion distilled between 183.5° and 184.5° , the boiling point of aniline. This portion was almost absolutely colourless, and gave on analysis the following results:—

0.4733 gram gave 1.3423 gram carbonic anhydride, and 0.3321 gram water.

These numbers lead to the formula NPhH_2 :—

	Calculated.		Found.
C_6	72	77.40	77.35
H_7	7	7.54	7.79
N	14	15.06	(14.86)
	93	100.00	100.00

The platinum salt was also prepared and analysed: 0.233 gram of the double salt contained 0.0756 gram platinum.

	Calculated for $\text{PtCl}_2\text{2NPhH}_2\text{Cl}$. In 100 parts.		Found.
Pt	3.29		3.24

The aniline was further identified by the purple coloration with chloride of lime, and by the isonitrile test.

It has been stated that a large volume of gas is evolved during this reaction, mixed, of course, with the vapour of ether. In order to procure this gas free from ether vapour, an experiment was performed in which azobenzene was added to pure zinc ethyl. Careful cooling was necessary in order to moderate the violence of the reaction. The gas was collected and submitted to eudiometric analysis, when the following results were obtained:—

	Tension (dry).	Temperature.
Original gas	174.2 mm.	18° C.
After action of SO ₃	45.2 „	„
Vol. of residual gas taken for combustion.....	18.9 „	„
After addition of O	117.0 „	„
After explosion	71.0 „	„
After absorption of CO ₂	32.8 „	„

These numbers show that 18.9 vols. of the gas taken for combustion consumed 65.3 vols. of oxygen, and generated 38.2 vols. of carbonic anhydride, numbers which correspond with the following proportions:—

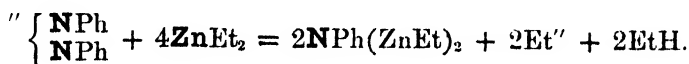
Vol. of comb. gas.	O consumed.	CO ₂ generated.
1 :	3.46 :	2.02

The gas left after the action of SO₃ is therefore ethylic hydride, and the original gas consists of—

C ₂ H ₄	25.95
C ₂ H ₆	74.05

100.00

The formation of aniline might be explained in the following manner:—In the first place the zinc ethyl severs the nitrogen-atoms of the azobenzene molecule, forming 2 mols. of dizincmonethyl aniline:—

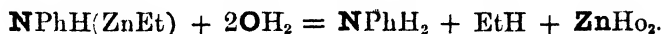
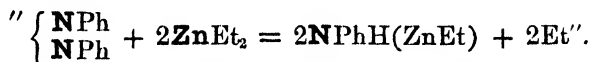


The dizincmonethyl aniline is then decomposed by water:—



If this explanation is correct, the gas which is evolved during the reaction must consist of equal volumes of ethylic hydride and ethylene, and each molecule of azobenzene must yield 2 mols. of aniline. The gaseous product of the reaction, however, has been shown to consist of 3 vols. of ethylene to 1 vol. of ethylic hydride, and it is therefore

probable that two-thirds of the base is formed by the following consecutive reactions :—



In a quantitative experiment 80 grams of azobenzene yielded 70 grams of aniline. Allowing for unavoidable loss, and taking into account the simultaneous formation of the substance of high boiling point already referred to, this result may be regarded as a satisfactory approximation. It shows clearly that more than half the azobenzene is converted into aniline. In all reactions as yet known in which aniline is formed from azobenzene, only half the azobenzene goes to form aniline. With some substituted azobenzenes the formation of 2 mols. of substituted anilines from each molecule of the substituted azobenzene may be accomplished by means of reducing agents, as, for example, in the case of the azo-colouring matters. The zinc ethyl reaction extends this total reduction to azobenzene itself.

The substance boiling above the range of the thermometer, the yield of which was about one-twentieth of the aniline, was redistilled under reduced pressure. It came over at about 260° under 160 millimeters' pressure of mercury. The distillate formed a clear yellow oil, which when cold was viscid, but did not solidify even in a freezing mixture. It dissolved in hydrochloric acid, but the solution turned rapidly dark-red, and when evaporated did not crystallise. When platinic chloride was added to the hydrochloric acid solution, metallic platinum was precipitated.

The smallness of the quantity at our disposal and the difficulties in the way of purifying this body caused us to abandon its investigation.

2. On the Action of Zinc Ethyl upon Benzonitrile.

By E. FRANKLAND, F.R.S., and JOHN CASTELL EVANS, Esq.

About equal parts by volume of zinc ethyl and benzonitrile were heated together in a sealed tube for some hours to 150°. On cooling the contents of the tube had solidified to a brownish mass. This was treated first with alcohol, in order to decompose the excess of zinc ethyl, and afterwards with hydrochloric acid, to remove the zinc hydrate. The substance which remained consisted of white needles, sparingly soluble in alcohol, but dissolving readily in carbonic disulphide. From hot saturated solutions, it was deposited in white ramiform needles fusing at 229°. These characteristics pointed to cyaphenine ($\text{C}_{21}\text{H}_{15}\text{N}_3$)—a substance first obtained by Cloëz (*Annalen*,

115, 27) by heating benzoyle chloride with potassic cyanate. Subsequently Engler (*Annalen*, **133**, 146) obtained the same compound by heating benzonitrile bromide, either alone or with lime. A. W. Hofmann (*Ber.*, **1**, 194) prepared it by the action of sodium on benzonitrile; E. Schmidt (*J. pr. Chem.* [2], **5**, 35), described the formation of traces in the action of carbonic oxydichloride on benzamide; whilst Pinner and Klein (*Ber.*, **11**, 764) discovered a method of obtaining it in large quantities by polymerising benzonitrile with fuming sulphuric acid.

The fusing point of cyaphenine is given by Cloëz at 224° , and by Pinner and Klein at 231° . Cyaphenine is, according to the above formula, a trimolecular benzonitrile, and is an aromatic analogue of the base cyanethine, first described by one of us in conjunction with Kolbe (*Chem. Soc. J.*, **1**, 60).

An experiment was then made to ascertain whether the reaction would take place under ordinary pressure. 60 grams of benzonitrile with an equal volume of zinc ethyl were heated in a flask fitted with a reversed condenser for some hours to the boiling point of the mixture. At first no change was apparent, but gradually the liquid assumed a reddish-brown colour; and, after the lapse of about four hours, a reaction commenced, accompanied by an evolution of gas. At the same time the contents of the flask became pasty. As soon as the gas ceased to be evolved an ordinary condenser was substituted for the reversed condenser, and the excess of zinc ethyl was distilled off. The product of the reaction was treated with alcohol and hydrochloric acid as above described, and in this way a large yield of cyaphenine was obtained. It was noticed that in decomposing the mass with alcohol a strong ammoniacal odour was evolved.

The cyaphenine was crystallised from hot carbonic disulphide, and the crystals were washed on the filter with cold alcohol, in which they are almost insoluble. In this way the substance was obtained perfectly pure and colourless after two crystallisations. Analysis yielded the following results:—

I. 0.3730 gram gave 1.1117 gram carbonic anhydride, and 0.1645 gram water.

II. 0.2278 gram gave 0.1152 gram ammonic chloride.

	Calculated for $(C_7H_5N)_3$.		Found.
C ₇	84	81.55	81.26
H ₅	5	4.85	4.90
N.....	14	13.60	13.23
	103	100.00	99.39

Cyaphenine may, as has been stated by former investigators, be boiled with caustic potash or hydrochloric acid without undergoing

change; but by heating it with concentrated hydrochloric acid in a sealed tube to 250° we have succeeded in converting it entirely into benzoic acid and ammonia.

The liquid obtained by treating the product of the zinc ethyl reaction (after decomposition by alcohol) with hydrochloric acid in order to remove the zinc hydrate, deposited on standing faintly greenish six-sided plates. The colour was removed by a single recrystallisation from very dilute alcohol. This substance proved to be the hydrochlorate of a base. It yielded on analysis the following results:—

I. 0.1869 gram gave 0.4722 gram carbonic anhydride and 0.1192 gram water.

II. 0.1112 gram gave 15.136 c.c. (calibrated volume) of dry nitrogen at 20° under 477 mm. pressure corresponding to 0.01112 gram.

III. 0.3748 gram gave 0.1962 gram argentic chloride.

These results lead to the formula $C_{16}H_{19}N_2Cl$:—

	Calculated.		Found.
C_{16}	192	69.95	69.89
H_{19}	19	6.92	7.30
N_2	28	10.20	10.00
Cl	35.5	12.93	12.95
	274.5	100.00	100.14

Another determination of carbon and nitrogen *in vacuo* gave C 70.02 and N 10.06 per cent.

The hydrochlorate dissolves readily in alcohol, but is very sparingly soluble in water, even at 100° . It fuses at 257° , and when heated much above its fusing point gives off an odour of benzonitrile. It yields with platinic chloride a very badly characterised platinum salt, which was not analysed.

The base separates out as a colourless oil on the addition of caustic alkali to the solution of the hydrochlorate.

We must reserve the further investigation of this compound until we have been able to obtain it in larger quantities.

The gas given off during the action of zinc ethyl on benzonitrile was collected and analysed; two experiments gave the following results:—

	I.	II.
Pressure of original gas 0° (dry) ..	58.3 mm.	44.2 mm.
„ after action of SO_3	28.4 „	22.7 „
„ „ addition of oxygen ..	175.9 „	197.2 „
„ „ explosion	105.3 „	139.9 „
„ „ absorption of CO_2	48.7 „	95.1 „

One volume of the combustible gas left after action of SO:—

	I.	II.	Mean.
Consumed	3·47	3·49	3·48 vols. of O.
Generated	1·99	1·97	1·98 vols. of CO ₂ .

1 vol. of ethylic hydride consumes 3·5 vols. of oxygen, and generates 2 vols. of carbonic anhydride. The gas therefore consists of an olefine (C_nH_{2n}) and ethylic hydride in the following percentage proportions:—

	I.	II.	Mean.
C _n H _{2n}	51·28	48·64	49·96
C ₂ H ₆	48·72	51·36	50·04
	100·00	100·00	100·00

No determination of the molecular composition of C_nH_{2n} was made, but there can be no doubt that its molecular formula is C₂H₄, and that the mixture of equal volumes of ethylene and ethylic hydride is produced by the very usual transformation of ethyl into equal volumes of these gases.

3. Action of Zinc Ethyl on Phenylacetoneitrile.*

By E. FRANKLAND, F.R.S., and HARRY K. TOMPKINS, Esq.

The phenylacetoneitrile employed in the following experiments was prepared by digesting benzylic chloride with a solution of crude potassic cyanide in dilute alcohol. The benzylic chloride was obtained by fractional distillation from a commercial product, and came over between 172—180°. The preparation of phenylacetoneitrile has been frequently described in detail (Cannizzaro, *Annalen*, **96**, 246; Radziszewski, *Ber.*, **3**, 198); we may, however, record an observation which seems not to have been made before. In one experiment on a large scale, in which 2,000 grams of benzylic chloride with an equal weight of potassic cyanide were employed, and the digestion was continued for about a week, we obtained, in addition to some unattacked benzylic chloride and a large yield of phenylacetoneitrile boiling between 200—230°, a considerable quantity of a substance distilling with decomposition above 300°. The distillation was therefore interrupted, and the retort allowed to cool, when the contents partially solidified to a mass

* In studying the action of zinc ethyl upon nitriles and cyanides, the following typical examples of these two classes of compounds have been selected:—Nitriles—acetoneitrile (fatty), benzonitrile (aromatic), phenylacetoneitrile (fatty aromatic). Cyanide—phenylic cyanide. Cyanide with acid radical—benzoyle cyanide. The results obtained with benzonitrile have already been communicated to the Society; in the case of acetoneitrile the work was unavoidably interrupted, but I have again taken it up in conjunction with Mr. Tompkins. With benzoyle cyanide Mr. D. A. Louis has obtained interesting results which are almost ready for publication.—E. F.

of lamellar crystals. These, after pressing from the adhering oily matters, were purified by crystallisation from hot alcohol. The substance was thus obtained in large colourless tabular crystals, sometimes more than an inch square, fusing at 92° . From *dilute* alcoholic solutions, the substance was deposited in needles. Analysis yielded results agreeing with the formula of tribenzylamine, to which substance the characteristics above described also pointed (see Limpricht, *Annalen*, **144**, 307). The formation of tribenzylamine by the action of an excess of benzylic chloride on the ammonia produced by the saponification of the potassic cyanide, needs no further comment.

We were unable to obtain phenylacetonitrile in a state of perfect purity. The fraction boiling between $200-230^{\circ}$ was distilled ten times and collected in fractions of from five to five degrees, but the thermometer showed no tendency to remain stationary at any point. The phenylacetonitrile was contaminated with some substance containing oxygen, as was shown by its giving off water every time it was distilled, however carefully it might have been dried.

An attempt was made to prepare pure phenylacetonitrile by distilling ammoniac phenylacetate with phosphoric anhydride, but nothing was obtained except an oil boiling above the range of the thermometer. The boiling point of phenylacetonitrile is given by Radziszewski at 229° .

We therefore employed in the following experiments the product boiling between $200-230^{\circ}$; but by saponifying a portion of it and obtaining a large yield of phenylacetic acid, we first satisfied ourselves that it consisted for the most part of the product sought.

Thirty grams of phenylacetonitrile with an equal weight of zinc ethyl, were introduced into a flask fitted with a wide tube intended to act as an inverted condenser. The reaction began spontaneously: the temperature of the mixture rose and gas was evolved. When the reaction became too violent, it was checked by immersing the flask in cold water. Care must be taken not to use too large quantities of the substances, otherwise the reaction is apt to become unmanageable. Towards the close, the mixture is heated in an oil-bath, the temperature of which is not allowed to exceed 130° . The operation must be carefully watched, as the mixture becomes viscid and is apt to froth. When gas ceases to be evolved, the flask is allowed to cool, and the product is decomposed with alcohol, in which process gas is evolved in great quantity. When the decomposition is complete, the contents of the flask are boiled with excess of alcohol and filtered hot. The residue is extracted a second time with hot alcohol, after which nothing but white oxide of zinc is left on the filter. The united filtrates deposit, on standing, a small quantity of a crystalline substance, the separation of which requires some days for its completion.

The crystals obtained from a number of such operations were united and recrystallised from hot alcohol. In this way two distinct substances were isolated from the crystalline product: the first crystallising in tufts of silky needles fusing at 170—171°; the second, which was obtained on further evaporation of the mother-liquor from the needles, separating in well-formed crystals, apparently rhombohedra, fusing at 150°. The rhombohedra were sometimes mixed with hexagonal plates which had the same fusing point, and, in all probability, belonged to the same crystalline system.

The needles yielded the following results on analysis:—

I. 0.1755 gram gave 0.5287 gram carbonic anhydride and 0.0974 gram water.

II. 0.0701 gram gave 6.263 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.007836 gram nitrogen.

III. 0.1342 gram gave 12.1 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.01514 gram nitrogen.

	Calculated.		Found.			
			I.	II.	III.	Mean.
C ₈	96	82.05	82.16	—	—	82.16
H ₇	7	5.98	6.16	—	—	6.16
N	14	11.97	—	11.17	11.27	11.22
	117	100.00	—	—	—	99.54

The substance employed in II and III had a yellowish tinge, and was not so pure as that used in I. The smallness of the quantity at our disposal precluded the possibility of a further purification.

The substance has thus the same empirical formula as phenylacetonitrile, from which, however, it differs in all its physical properties. The formula must probably be tripled in accordance with the analogy of the trimolecular nitriles, cyanmethine and cyanethine. The molecular formula of cyaphenine rests entirely on a similar analogy. The present compound would be the fourth known member of this class, and the name to be assigned to it would be *cyanbenzine*.

It would probably be possible to determine the molecular weight of cyanbenzine on surer grounds than those of analogy, inasmuch as it appears to form salts. When treated with warm dilute hydrochloric acid, it forms a gummy mass—probably a hydrochlorate. The small quantity of substance at our disposal, the yield not being more than one per cent. of the phenylacetonitrile employed, rendered it impossible for us to extend our investigations in the direction of the salts of cyanbenzine.

Cyanbenzine is sparingly soluble in hot, almost insoluble in cold alcohol. Glacial acetic acid, benzene, and carbonic disulphide dissolve it readily.

This polymerising action of zinc ethyl was also observed in the case of benzonitrile, and has been described in a former communication.

The following results were obtained in the analysis of the rhombohedral crystals:—

I. 0.2816 gram gave 0.8397 gram carbonic anhydride and 0.1473 gram water.

II. 0.2206 gram gave 0.6590 gram carbonic anhydride and 0.1166 gram water.

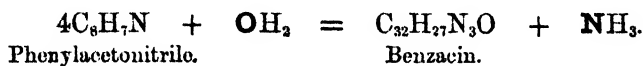
III. 0.1073 gram gave 7.635 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.009551 gram nitrogen.

IV. 0.0783 gram gave 5.598 c.c. (corr. vol.) nitrogen at 0° and under 760 mm. pressure, corresponding to 0.007004 gram nitrogen.

These data agree with the formula $C_{32}H_{27}N_3O$, as is seen from the following comparison:—

	Calculated.		Found.				
			I.	II.	III.	IV.	Mean.
C_{32}	384	81.88	81.32	81.47	—	—	81.39
H_{27}	27	5.75	5.81	5.87	—	—	5.84
N_3	42	8.96	—	—	8.90	8.94	8.92
O	16	3.41	—	—	—	—	(3.85)
	469	100.00	—	—	—	—	100.00

The formation of the substance, $C_{32}H_{27}N_3O$, for which we propose the name *benzacin*, may be explained by the equation—



Benzacin is a neutral body. We are not in a position to offer any suggestions as to its constitution, and till some method has been discovered by which it can be obtained in greater quantity, a study of its reactions must remain a practical impossibility.

The filtrate from the first crop of mixed crystals, containing all the other soluble matters from the zinc ethyl reaction, was next examined. On distilling off the alcohol, a large quantity of a neutral oil of high boiling point was left, which when cold was viscid, but did not show any tendency to solidify, even after standing for some days in an ice safe. On attempting to distil this oil, it first gave off a small quantity of unchanged phenylacetonitrile; after which the temperature rose suddenly, and the residue distilled with decomposition above the range of the thermometer. An attempt to rectify this liquid *in vacuo* failed, owing to the constant evolution of salts of ammonia, which choked the condenser and rendered the operation dangerous.

As the oil contained nitrogen, we thought it possible that we might be dealing with a nitrile, and boiled it with alcoholic potash, in the hope of obtaining the corresponding acid; but the oil was recovered from the operation apparently unchanged. Not being able to find any method of purifying this substance, or of preparing any well characterised derivative from it, we abandoned its investigation.

XLV.—*On a New Method of preparing Dinitroethylic Acid.*

By E. FRANKLAND, F.R.S., and C. COLBORNE GRAHAM, Esq.

THE method first described by one of us (*Phil. Trans.*, **147**, 59) of preparing dinitroethylic acid (N_2EtOHO) by the action of zinc ethyl upon nitric oxide was difficult and inconvenient. Owing to the slowness with which zinc ethyl absorbs nitric oxide at ordinary pressures, it was necessary to work with the gas at a pressure of 20 atmospheres. The zinc-ethyl was contained in a copper digester, into which the nitric oxide was forced by means of a condensing syringe. Probably the difficulty of preparing it has prevented any further investigation of this singular compound, since its first discovery a quarter of a century ago. The method we are about to describe is based on the superior reactivity of sodic ethide, which effects a rapid absorption of nitric oxide at ordinary pressures, and renders possible the preparation of considerable quantities of dinitroethylic acid in a short time.

In our first experiments, thoroughly dried nitric oxide was passed into a flask containing the double compound of sodic ethide and zinc ethyl. This method was found not to work well; the double compound soon solidified, and was acted on only superficially by the nitric oxide. By employing less sodium than was required for the complete conversion of the zinc ethyl into the double compound, the fluidity of the mass was to some extent preserved; but even then the contents of the flask became pasty towards the close of the reaction, and the process was both tedious and wasteful. In addition to this, two explosions, one of them very violent, convinced us that it had the further disadvantage of being dangerous.

It seemed to us that all these disadvantages might be removed if a suitable solvent for the double compound could be found. Benzene was tried and was found to answer admirably, as it dissolved the substance readily, and was neither so volatile as to be carried away in any quantity by the indifferent gases, which had to be let off from time to time, nor of so high a boiling point as to present difficulties in the way

of getting rid of it when necessary. The benzene solution of zinc-sodic ethide lends itself to all the reactions of the undissolved substance, absorbing carbonic anhydride and carbonic oxide, the latter however, but slowly. It will probably be a convenient form in which to employ this otherwise rather unmanageable reagent.

The method which we have finally adopted for the preparation of dinitroethylic acid is as follows:—

100 grams of pure zinc ethyl are introduced into a tubulated distilling flask and a quantity of sodium sufficient for the conversion of the whole of the zinc ethyl into the compound ZnNaEt_2 is added in thin slices. The flask must be immersed in water whenever the temperature shows a tendency to rise too high. A neglect of this precaution when working on this large scale may lead to loss, the heat evolved by the exchange of sodium for zinc being sufficient to boil off the zinc ethyl and totally destroy the product. When the action is complete, the contents of the flask will, if allowed to stand, solidify to a crystalline mass of zinc-sodic ethide. 100 c.c. of benzene are now added. The flask is fitted with a cork, through which passes a wide glass tube, reaching to within about an inch of the surface of the liquid, and serving for the introduction of the nitric oxide. The tube must be straight, so that in case of stoppage, it may be instantly cleared by passing a wire through it. To the tubulure of the flask is attached a short piece of black caoutchouc tubing closed by a clip, this opening being intended for the escape of unabsorbed gases. During the operation, the flask is wrapped in cloths and immersed in water. Pure nitric oxide, generated from nitre, ferrous sulphate, and dilute sulphuric acid, and collected in a glass gasholder, is thoroughly dried by passing through concentrated sulphuric acid, and is led through the wide glass tube into the flask containing the benzene solution of zinc-sodic ethide. Absorption takes place rapidly, and is further aided by shaking the flask. When it ceases owing to the accumulation of neutral gases (principally ethylic hydride, the formation of which is due to the presence of a trace of moisture in the nitric oxide), the clip is opened, and a rapid current of nitric oxide is sent through the apparatus. A sheet of white paper, placed behind the end of the exit tube, shows the escape of the nitric oxide by the formation of red fumes, upon which the tube is closed by the clip, and the absorption, aided by shaking, goes on as before. In this way about four liters of gas can be passed into the apparatus in the course of an hour. Towards the close, however, the absorption is more sluggish. If the mass becomes too pasty, more benzene may be added. As soon as the absorption has practically ceased, the flask is disconnected and ordinary commercial ether added to the contents, the flask being kept cool. This liquid contains sufficient alcohol and water to decompose

the excess of zinc ethyl in the mixture. The action of water, or even of alcohol, alone is too violent, and is apt to destroy a portion of the product. After a considerable quantity of ether has been employed and the action has begun to slacken, a little alcohol is gradually added. Finally, the decomposition is completed by means of an excess of water. Carbonic anhydride is then passed into the solution containing the precipitate of zincic hydrate. By this means both the free caustic alkali and the zincic hydrate are converted into carbonates, the former being thus prevented from exercising any destructive influence on the dinitroethylic acid during the subsequent evaporation, whilst the latter can be more readily filtered off. The liquid is now filtered roughly through calico, and the precipitate of zincic carbonate is carefully washed. The filtrate is evaporated to dryness and the mixed salts extracted with absolute alcohol, which dissolves only the sodic dinitroethylate. On evaporating the alcoholic solution, the latter salt remains as a crystalline deliquescent mass. The sodium salt is then converted into the copper salt, which, from its admirable crystalline properties, can readily be obtained in a state of perfect purity. For this purpose the sodium salt is dissolved in a small quantity of water, and an excess of concentrated solution of cupric sulphate is added. The mixed solution is evaporated nearly to dryness, the operation being best performed *in vacuo* in order to avoid decomposing the copper salt. On extracting with alcohol, a solution of almost pure cupric dinitroethylate is obtained, which, on evaporation, yields the characteristic large dark blue flat needles of this salt.

In some carefully conducted experiments, a yield of 50 per cent. of the theoretical quantity of the pure copper salt, calculating from the weight of sodium employed, was obtained.

We intend to study the reactions of dinitroethylic acid with a view to throw light upon its constitution.

XLVI.—*The Detection of Foreign Colouring Matters in Wine.*

By A. DUPRÉ, Ph.D., F.R.S.

IN January, 1876, I showed (*Analyst*, No. 2, p. 26), in a short note read before the Society of Public Analysts, that the true colouring matter of wine dialysed but very slowly, if at all, through parchment paper; whereas, on the other hand, various colouring matters, alleged to be used in the fraudulent coloration of wine, dialysed freely. A year later (*Analyst*, No. 11, p. 186) I showed that small cubes* of

* These cubes, about three-quarters of an inch side, are cut with a sharp wet

jelly, placed in the wine to be tested, could be substituted with advantage for the parchment paper. If, after a shorter or longer interval of immersion, such a cube is taken out, washed a little with water, and a central slice is cut out of it, in a direction parallel with one of the sides of the cube, it will be found, in case the wine be pure, that the colour has penetrated but a very little way into the cube (in the course of 24 to 48 hours the colour penetrates perhaps one-sixteenth of an inch), whereas many other colouring matters will have penetrated to the very centre of the cube.

Since then I have extended my examination, and have now, I believe, included all the more important colouring matters said to be used in the fraudulent coloration of wines, and several others besides. The broad fact, established formerly, remains unaltered, namely, that the colouring matter of pure wine and that of alkanet root (in the papers quoted rhatany root is printed in mistake) dialyse but very slowly into the jelly, while all the rest among those examined dialyse more or less rapidly. A wine, the colouring matter of which does not dialyse readily, is therefore presumably pure, or has only to be tested for alkanet root, while, if it dialyses readily, it must be pronounced impure; that is, artificially coloured. Fortunately, the colouring matter of alkanet root is readily distinguished from the colour of pure wine, and is, moreover, on account of its somewhat unstable character, not likely to be used. The colouring matter of a pure red wine shows a general absorption of light in all colours except the red, but, generally, no distinct absorption band. The red colour changes to a greenish-brown on addition of ammonia, becomes much darker in tint, and now shows a somewhat indistinct absorption band in the yellow and orange, besides the general absorption of everything except the red. The colouring matter of alkanet root shows, in an acid solution and of suitable concentration, three distinct absorption bands lying between the yellow sodium and the blue strontium lines, nearly equidistant from each other and from these lines. Ammonia turns the colour beautifully blue, and reduces the absorption bands to two, lying one over the sodium line, the other between that and the red lithium line, about two-thirds of the interval between these from the former. Both acid and alkaline solutions show a general absorption of the blue end of the spectrum, and indeed in moderately concentrated solutions absorb everything but the red.

In many cases it will be sufficient to show that the wine is artificially coloured, though sometimes it is necessary or desirable to go further. In such case the colour of the slice, or its absorption spectrum, or the action of ammonia on it, may lead to the discovery knife out of a plate of jelly of proper thickness, which can readily be cast in a paper mould of suitable size.

of the particular colouring matter present. As a general rule, the slice shows the proper colour of the added substance much more clearly than the wine itself. Indeed, it is a strong proof of the presence of a foreign colouring matter in a red wine if the colour shown by the slice differs from that of the wine. Indigo or logwood, for example, are thus readily discovered. The slice will also frequently furnish good results when examined by the spectroscope, as in the case of rosaniline, cochineal, beetroot, red cabbage, &c., &c. Lastly, the action of ammonia on the slice may yield characteristic results. Thus, a rosaniline slice, placed into diluted ammonia, becomes colourless; a red cabbage slice, dark green; a cochineal slice, purple; a logwood slice, brown. This latter effect, *i.e.*, a browning of the slice, is, however, frequently observed even if no trace of logwood is present, but with a little care this need not cause any difficulty. Tannin, which is always present in red wines, dialyses readily, and a gelatine slice cut from a cube which had been immersed in a pure wine, rich in tannin, gradually assumes a brown coloration when placed into ammonia. In these cases, however, the slice is colourless or nearly so, except close round its margin, as only the unoxidised tannin dialyses, and this nearly colourless slice gradually becomes brown. In the presence of logwood, this slice is coloured yellow or brown, to a considerable depth, before it has been acted on by ammonia.

If the nature of the foreign colouring matter present cannot be made out by these simple means, the wine must be submitted to a careful spectroscopic examination (*see* W. W. Vogel, *Ber.*, 1875, 1246), or be examined by the various precipitation and other tests described by Gauthier and others (*Bull. Soc. Chim.* [2], 25, 435—445, and *Chem. Soc. J.*, 1876 [2], 330). If these fail, as in my experience they very often do, more particularly if the wine under examination owes part at least of its colour to the true colouring matter of the grape, the following process may be adopted:—A foreign colouring matter having been proved to be present by means of the cubes of jelly, a larger quantity of the wine is submitted to dialysis in a parchment paper dialyser. When a sufficient amount of colouring matter has dialysed, the liquid may be examined, either directly or after careful concentration, by the spectroscope or chemically, and will now be found to answer to these tests uninfluenced, or nearly so, by the colouring matter of the grape, as this has remained inside the dialyser.

Formerly I employed jelly made with five parts of gelatine to 95 parts of water, but I find that in warm summer weather the jelly so made is not of sufficient solidity for use, and I now cut the cubes from a jelly containing 10 per cent. of air-dry gelatine.*

* I have quite recently been informed by Mr. Stansell that a jelly containing 10

The following are the colouring matters examined:—

Group a. Colouring matters that penetrate but slowly into the jelly:—

Colouring matter of pure wine.

„ „ alkanet root.

Group b. Colouring matters that penetrate rapidly into the jelly:—

<i>Althea officinalis.</i>	Currants, black.
„ <i>rosea</i> (hollyhock).	Elderberry.
Beetroot.	Indigo.
Bilberry.	Litmus.
Brazil wood.	Logwood.
Carnations (<i>Dianthus</i> <i>caryophyllus</i>).	<i>Malva sylvestris</i> .
Cherry, red, sour.	Raspberries.
„ black.	Red cabbage.
Clematis (purple).	Red poppy.
Cochineal.	Rhatany root.
Cranberry.	Rosaniline.
Currants, red.	Saffron.
	Strawberry.

In most cases an addition of colouring matter, equal to 10 per cent. of the total intensity of the colour of the wine, yields distinct results with these cubes. In some cases, as with logwood, 5 per cent., and in the case of rosaniline, even as little as 1 per cent. can be detected. In no case, I believe, could 20 per cent. (or four parts of wine with one part of a solution of the same depth of colour as the wine) be overlooked. It may be useful to state that, to the naked eye at least, the colour of the froth produced by shaking the wine is apparently influenced to a much greater degree by the presence of many of the above-mentioned colouring matters than that of the wine itself. If, therefore, a suspected wine yields a froth of like colour with a genuine wine of the same class, the presumption is in favour of its not being artificially coloured.

In conclusion, I would remark that if in the examination of a suspected sample of wine, the degree of dialysis shown seems somewhat great, though not sufficiently so to remove all doubt on the subject as to its purity or otherwise, it is advisable to procure a pure sample of a similar wine for direct comparison, when all doubt will generally be dispelled.

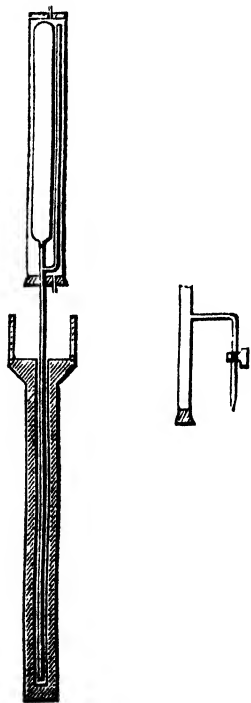
per cent. of glycerin, such as is used by microscopists, answers well, in some cases at least, and should it be found to answer generally it would have the great advantage that it will keep for a considerable length of time, and cubes cut from it could always be kept ready to hand.

XLVII.—*On a Simple Method of Determining Vapour-densities in the Barometric Vacuum.*

By CHICHESTER A. BELL, A.B. and M.B., and FRANK L. TEED, F.C.S.

IN spite of the great degree of simplicity to which the determination of vapour-densities has recently been brought by Meyer and others, there still remain many cases, *e.g.*, those of easily decomposable substances of high boiling point, and substances attacked by oxygen, in which the older method of Hofmann would be preferable. It has been shown, too, that to volatilise most liquids in a vacuum a temperature of 100° is sufficient; and as this temperature is rapidly attained and easily kept constant for any length of time, this fact is strongly in favour of Hofmann's method.

In the following modifications of Hofmann's apparatus, two new devices are introduced. Firstly, by varying the external pressure or otherwise, the vapour is made to occupy a known volume; and, secondly, its pressure is directly determined by a single observation, which is independent of the atmospheric pressure. The calculations are thus enormously simplified, and no room is left for errors of observation.



The simplest form of our apparatus, which we have adopted after many experiments, consists of an experimental cylinder and a steam-jacket. The first is composed of a glass cylinder 34 cm. long and 3.3 cm. in internal diameter, closed at one end, and at the other fused on to a stout glass tube 8 mm. in internal diameter, and about 83 cm. in length. 5 cm. below the junction a second tube of nearly the same diameter is fused into the latter at right angles. This tube, which serves as a barometer, is then bent upwards so as to be parallel and close to the cylinder, and is sealed off about 1 cm. below its upper end. The lower end of the long stem is provided with a well-fitting india-rubber cork, through the centre of which passes a short glass tube of narrow bore provided with an air-tight stop-cock. This tube may also with advantage be fused into the

long stem a little above its end, in which case the stem is closed with a plain india-rubber cork.

About 1 cm. below its junction with the cylinder a fine line is etched on the stem, and from a point on exactly the same level the barometer is graduated upwards in millimeters, the graduation being continued for a few millimeters below the zero point. If a cathetometer is available this graduation is unnecessary.

The steam-jacket consists of a glass cylinder sufficiently wide and long to pass easily over, and completely envelop, the cylinder and barometer. The upper end of this may be closed with a perforated cork, carrying a tube to admit the heating vapour. The lower end is closed with a doubly perforated cork (preferably of india-rubber). Through one hole passes the stem of the cylinder; the other is filled by a tube which serves to carry off the heating vapour. When in use the lower cork rests on the ring of a retort stand, which thus supports the whole apparatus.

The volume of the cylinder down to the line on the stem is once for all accurately determined, and the weight of hydrogen (or air) which it could contain at 100° and 10 mm. pressure of mercury at 100° calculated, due allowance being made for the expansion of the glass. This weight may be called the *constant* of the apparatus. It will be convenient to calculate its value for several half-degrees above and below 100° . Should other heating vapours than steam be used, the value of the constant should be determined for 100° absolute temperature, and 10 mm. pressure of mercury at 0° .

The depression of mercury in the barometer below that in the stem due to capillarity, may be either calculated or experimentally determined. The correction for this may be made to include any error in fixing the zero point of the scale.

To make an experiment, the cylinder, barometer, and stem are first completely filled with mercury, air bubbles being removed as far as possible. The substance, sealed up in a small bulb which it almost fills, is then placed on the surface of the mercury at the mouth of the stem, and pressed down by the india-rubber cork, which is then screwed firmly home, the stop-cock being in the meantime open. The stop-cock is then closed, the cylinder held vertically, and mercury allowed to flow out through the tap until communication is established between the cylinder and barometer, by which means any traces of air are uniformly distributed.

By now immersing the beak of the tap in some mercury and inclining the apparatus, the metal may be caused to rise again until it occupies the lower sixth of the cylinder. If this be done gradually there is no risk of air entering from the joint of the stop-cock or cork. The stop-cock is now closed, the apparatus and cork placed on the

ring of the retort stand, the steam-jacket adjusted, and the heating vapour passed through it. The bulb having burst, and a uniform temperature having been obtained, the barometer is held in a strictly vertical position, and mercury again allowed to escape until its level sinks exactly to the mark on the stem. The height of the column in the barometer tube, corrected if necessary for capillarity, now gives the pressure of the vapour; and by dividing the weight of the substance by the constant multiplied by the pressure expressed in centimeters of mercury, we at once get the density of the vapour referred to hydrogen or air. When a heating vapour other than steam is used the method of calculation is obvious. The manipulation of this apparatus is exceedingly simple: and as a comparatively small quantity of mercury is rendered impure at each experiment, a number of determinations may be made in a comparatively short time.

The only source of error lies in the change in volume, and therefore in pressure, of the small quantity of air in the barometer, owing to the rise of the mercury. This, however, is scarcely perceptible, and might be rendered absolutely inappreciable by expanding the upper end of the barometer tube into a bulb.

Another form of apparatus which has certain advantages, though by no means so easily manipulated as the above, comprises, in addition to the parts already described, a mercury trough made of dense wood. This has a circular bowl about 10 cm. in diameter and 7 cm. deep, prolonged below into a tube about 25 mm. in diameter and 50 cm. deep. The india-rubber cork and stop-cock of the stem are dispensed with. To make an experiment the trough, resting on the ground, is partly filled with mercury. The cylinder is also filled as before, the mouth of the stem closed by the finger, inverted in the mercury in the trough, and supported in a vertical position by the cork of the steam-jacket which rests on the ring of a weighted retort-stand placed at the edge of a table. The weighed bulb having been introduced, communication between the cylinder and barometer is made by raising the experimental tube. The latter is then lowered until the cylinder is half-full of mercury, the jacket adjusted, and vapour injected. The mercury having been thoroughly heated and the liquid vaporised, the cylinder is raised until the vapour occupies the proper volume, the rest of the operation being conducted as before. It would of course be easy to construct a support, more or less elaborate, to suit the fancy of the operator, which would serve the same purpose as the retort-stand.

In addition to the advantages already mentioned, these methods have another which may be of considerable importance. Brühl (*Ber.*, 12, 197) has shown that at temperatures above 180° the tension of mercury vapour becomes so considerable as to render the results obtained by Hofmann's method exceedingly inaccurate. Although we

have not as yet used our apparatus at high temperatures, this objection would obviously not apply to it, since the mercury in the cylinder and that in the barometer would be equally depressed.

How far these devices may be of use in facilitating the measurement of vapour-tensions, we intend to make the subject of special experiment.

The following are some of the results obtained by means of this apparatus:—

Temperature in all cases 100° C.

Cylinder A. Capacity = 282.3 c.c. Capillarity = 2.5 mm. Constant = 0.0024512.

Body.	Weight in grams.	Pressure in c.m.	Vapour- density (found).	Vapour- density (calculated).	Vapour-density (other observers).
Benzene	0.122	12.35	40.3	39.0	40.2
Pyrrrol	0.0883	10.7	33.7	33.5	34.7
Water	0.046	20.65	9.1	9.0	9.0
Amyl iodide . . .	0.1974	7.7	104.6	99.0	96.5
Amyl alcohol . .	0.083	7.6	44.5	44.0	45.5

Cylinder B. Capacity = 313.4 c.c. Capillarity = 1 mm. Constant = 0.002654.

Amyl iodide . . .	0.1509	5.63	101.0	99.0	96.5
Water	0.046	19.0	9.1	9.0	9.0
Butyric ether . .	0.0771	4.9	59.3	58.0	58.4

The numbers in the last column are taken from *Watts's Dictionary*; the numbers there given being referred to air as unity, have been multiplied by 14.45.

The column headed "pressure" gives the observed pressure plus the capillarity.

XLVIII.—On a Crystal of Diamond.

By HARRY BAKER, Dalton Scholar in the Chemical Laboratories of
The Owens College.

THE following description of a South African diamond crystal in possession of Dr. Roscoe, may prove worthy of record as showing clearly by the total absence of tetartohedral edges, its holo- and not hemihedral nature. The holohedrae of the diamond has been pointed out

by Hirschwald (*Zeit. f. Kryst.*, i, 212), and again by Sadebeck (*Zeit. f. Kryst.*, ii, 93), who refers the grooved edges to a laminated growth of the crystal.

The stone in question is perfectly colourless and transparent, has a diameter of 5 mm., and a weight of 0.248 gram. Fig. 1 represents it as truthfully as possible, while Fig. 2 shows the ideal crystal. The whole consists of eight individuals arranged in parallel position about a common centre; and with the exception of the two lying at the back of Fig. 1, are of very nearly equal size. Of each of the individuals, as nearly as possible one-half of the whole crystal is developed, so that the re-entering angles between the individuals, and still more the

FIG 1.

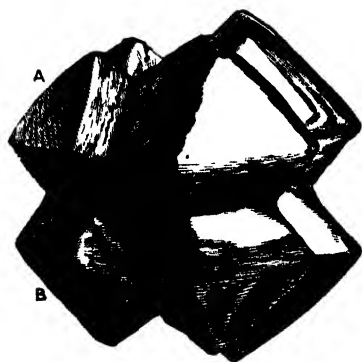
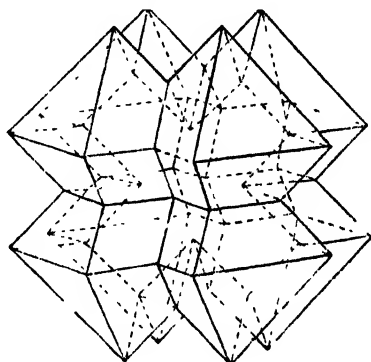


FIG. 2.



little hollows at each of the octohedral corners, where four individuals meet, are very deep.

The only faces developed sufficiently well to allow of measurements being taken, are those of the octohedron; but these are exceedingly perfect, and allow of exact measurement. The following angles were measured on four faces lying in a zone, viz., A, B, and the two opposite faces (A) and (B):—

$$\begin{aligned} A : B &= 109^{\circ} 28'7'' \\ (A) : (B) &= 109 \quad 29 \\ A : (B) &= 70 \quad 31.5 \end{aligned}$$

The angles are so near those required theoretically, viz., $109^{\circ} 28'2''$ and $70^{\circ} 31'8''$, that the individuals must be considered as perfectly parallel.

All the octohedral edges are roughly rounded off, apparently by a hexakisoctohedron, which is in oscillatory combination with the octohedron. Thus the outer portions, at least, of all the individuals would seem to be built up of numerous laminæ. Owing to this replacement of the octohedral edges, the smaller faces lying between the different

individuals are for the most part more or less completely obliterated, but nevertheless several of these small faces, both in the furrows along the octohedral edges and the depressions at the octohedral corners, are developed as perfectly as the large faces lying in the outer octants.

One other point is noticeable, namely, that on most of the larger outlying octohedral faces there are several more or less large triangular-shaped depressions, whose bounding edges are reversed to those of the face in which they lie, *i.e.*, parallel to the bounding edges of the opposite octohedral face. In consequence of this the crystal shows asterism, and a bright flame viewed through two opposite faces of the crystal is seen to be surrounded by six rays cutting each other at 60° .

XLIX.—On some Higher Oxides of Manganese and their Hydrates.

By V. H. VELEY, B.A., Christ Church Laboratory, Oxford.

Preliminary Discussion.

THE higher oxides of manganese have within the last few years received much attention from chemists. It has been shown that when oxides are prepared by methods in which alkalis take part, such as the action of potassium permanganate on a salt of the protoxide of manganese, reduction of the permanganate, or precipitation of the higher chloride with salts of the alkalis, then the oxides carry down with them, probably in combination, an appreciable quantity of the alkali (Fresenius, *Zeits. Anal. Chem.*, 1872, 295; Wright and Menke, *Chem. Soc. J.*, 1880, 22—48). It seemed that a study of higher oxides, prepared so as to avoid all possible contamination with alkali, was still desirable, and that it was most probable that an oxide so prepared might possess properties differing from alkali containing products.

Görgen (*Ann. Chim. Phys.* [3], 66, 153) described a series of derivatives of a manganous acid, $\text{H}_2\text{O}, 5\text{MnO}_2$, in which the hydrogen may be replaced by potassium, calcium, or manganese itself. This latter body, $\text{MnO}, 5\text{MnO}_2$, was prepared (1) by passing a current of chlorine for several hours through water in which manganese carbonate was suspended; (2) by dropping potassium permanganate slowly into a solution of manganese chloride, the oxide being formed according to this reaction—



It is very probable that the latter process led to the production of an

alkaline oxide. Somewhat later G6rgen (*Bull. Soc. Chim.*, 1864, **1**, 90) classified the higher oxides of manganese as manganese salts of manganic and permanganic acids, the oxide, $5\text{MnO}_2, \text{MnO} = \text{Mn}_6\text{O}_{11}$, being represented as $4\text{MnO}, \text{Mn}_2\text{O}_7$, thus comparable with $3\text{MnO}, \text{Mn}_2\text{O}_7 = 5\text{MnO}_2$. The pure dioxide can only be prepared by heating the nitrate to a temperature of $155\text{--}162^\circ \text{C}$. (*Compt. rend.*, **88**, 769), the artificial product resembling in appearance and physical properties the native mineral polianite.

Wright and Menke (*loc. cit. supra.*) repeated these experiments.

G6rgen's oxide, $5\text{MnO}_2, \text{MnO}$, is the subject of the present paper.

Preparation of the Substance.

A hundred grams of manganese chloride were dissolved in a litre of water, 10 c.c. of concentrated hydrogen chloride were added, and a slow current of sulphuretted hydrogen passed, a small quantity of a dark precipitate was formed and separated by filtration. The excess of the sulphuretted hydrogen was boiled off and a little chlorine water added, and the liquid warmed to secure the peroxidation of any iron salt which might be present. To this ammonium hydrate was added to incipient precipitation, and the liquid filtered; in the precipitate so obtained were appreciable quantities of iron. The manganese was then precipitated as the hydrated pink manganese sulphide with yellow ammonium sulphide, washed at first by decantation, and afterwards on the filter with a dilute (about 10 per cent.) sulphuretted hydrogen solution to prevent oxidation. The sulphide was then dissolved in freshly redistilled acetic acid to rid it of any sulphides of zinc, nickel, and cobalt which it might contain. The solution partially evaporated down to expel the H_2S gas, was diluted with three or four times its bulk of distilled water, and chlorine passed through for a limited time at a temperature of $52\text{--}53^\circ \text{C}$. Black glistening scales of the higher oxide were obtained, which were washed until the washings gave no precipitate with silver nitrate, nor any acid reaction with litmus paper; finally, it was air dried at $30\text{--}40^\circ \text{C}$. By these means the higher oxide was freed from the heavy metals and the alkalis.

Method of Analyses.

(1.) *Determination of the Water.*—The oxide was heated in a current of air or oxygen, purified, and dried by passing through (i) a wash-bottle containing soda solution; (ii) a U-tube containing freshly ignited pumice moistened with concentrated soda solution; (iii) a wash-bottle containing strong sulphuric acid; (iv) a U-tube filled with small fragments of potash; (v) a U-tube filled with pumice moistened with strong sulphuric acid; (vi) a drying tower similarly filled. The

various parts of the apparatus were refilled from time to time in the course of the experiments. The air thus purified was drawn through a piece of combustion tubing in which was placed a platinum boat containing the oxide. The tube was enclosed in an air-bath, the temperature of which was registered by a thermometer, and the pressure of the gas used for heating it being regulated by a gas regulator. The water given off by the oxide was collected by a U-tube (of the form used in combustion analyses) containing pumice moistened with the same sulphuric acid as that in the former part of the apparatus. To ensure accuracy the collecting tube was counterpoised by a similar tube on the opposite pan of the balance. To test the drying apparatus and collecting tube many blank experiments were made before and during the analyses, of which the following may be mentioned :—

Condition.	Time.	Temp.	Gain in tube.	Remarks.
Blank	14 hours	200° C.	Nil	Rate of air about 400 c.c. per hour.
Do.	16 "	200° C.	0·0006	
Do.	2½ "	Low redness	Nil	Oxygen used instead of air.

Determination of the Oxygen (beyond that contained in the Protoxide).

This so-called available oxygen was estimated either by Bunsen's process of distillation, or in the following manner:—A weighed quantity of the oxide was brought into a known volume of potassic iodide contained in a stoppered bottle, a known volume of hydrogen chloride added, the mixture diluted, and the bottle closed and kept in a warm place; at the same time a blank experiment was made with the same volumes of potassic iodide and hydrogen chloride of the same strength, and kept under the same conditions. The iodine liberated was estimated by a sodic thiosulphate solution, which was standardised by iodine, re-sublimed over iodide of potassium, and dried, and also with freshly recrystallised potassium bichromate, heated nearly to its fusing point.

The values obtained were—

(1.) By iodine.	(2.) By bichromate.
I per 1 c.c. $\left\{ \begin{array}{l} 0\cdot007824 \text{ gram.} \\ 0\cdot007825 \text{ " } \\ 0\cdot007827 \text{ " } \end{array} \right.$	I per 1 c.c. $\left\{ \begin{array}{l} 0\cdot007823 \text{ gram.} \\ 0\cdot007800 \text{ " } \\ 0\cdot007799 \text{ " } \end{array} \right.$

The mean value from these results may be taken as 007820 gram iodine per 1 c.c., corresponding to 0004932 oxygen.

* These processes are designated by the letters (a) and (b).

Determination of the Manganese Monoxide.

The higher oxide was heated in a current of hydrogen until the weight of the green manganese monoxide was constant. It was found that the higher the temperature at which the reduction was effected, the less liable was the monoxide to subsequent oxidation; in fact, specimens reduced at a higher temperature were kept for several weeks in a closely stoppered tube without appreciably altering in colour.

Atomic weights used: Manganese, 54·8; oxygen, 15·96; hydrogen, 1.

Analyses of the oxide when air dried at 30—40° C. :—

	Values obtained.	Mean.	Calculated for $3(5\text{MnO}_2\text{MnO})10\text{H}_2\text{O}$.
Manganese monoxide..	75·39, 75·31, 75·40	75·37	75·25
Oxygen	14·05 (a), 14·08 (b)	14·06	14·14
Water	10·51, 10·55	10·54	10·61
		99·97	100·00

The ratio between the manganese monoxide and oxygen is very nearly that of Görgen's formula, 5MnO_2 to MnO ; but the number of molecules of water is not integral for the formula, being about $3\frac{1}{3}\text{H}_2\text{O}$. The whole substance can be represented thus, $3(5\text{MnO}_2\text{MnO})10\text{H}_2\text{O}$; probably it is either $\text{MnO}5\text{MnO}_2\cdot3\text{H}_2\text{O}$ incompletely dried, or MnO , 5MnO_2 , $4\text{H}_2\text{O}$ a little over-dried and dehydrated.

Composition of the Substance after being Heated in Air to 200—250° C.

It was found in several series of analyses of the oxide (i) that at temperatures between 210—250° C., a point was reached at which the oxide did not lose weight, even when heated for several hours; (ii) that the loss of the oxide as deduced from the weighings of the boat with its contents did not agree with the gain in weight of the drying tube; (iii) that the oxide when dried at this temperature lost on ignition a further quantity of water; this last fact has previously been observed by Wright and Menke, Pickering and others.

The substance when constant at 200—250° C. was analysed with the following results:—

	Values obtained.	Mean.	Calculated for $\text{MnO} \cdot 11\text{MnO}_2 \cdot \text{H}_2\text{O}$.
Manganese monoxide..	81·30, 81·51, 81·63	81·48	81·44
Oxygen	16·89 (a), 16·73, 16·77 (b)	16·79	16·84
Water	1·68, 1·70	1·69	1·72
		99·96	100·00

Experiments by Pickering (*Chem. Soc. J.*, 1879, **35**, 659) apparently proved that moist oxides, poor in oxygen, absorbed oxygen, while oxides rich in oxygen lost oxygen, both reactions increasing in extent up to 200—250° C.

In fact the net result of heating the substance up to 200° C. in dry air is expressed by the following equation:—



That this is really so is shown by the following results:—

1. By the loss of the original substance when heated to 200° C. until the weight was constant.

TABLE I.

Condition.	Time.	Temperature.	Weight of oxide.	Loss.	H ₂ O coll.	Flow of air.
—	—	—	0·3779	—	—	—
Heated in a } slow current of air }	5 hours	200—210° C.	0·3497	0·0282	0·0333	{ 400 c.c. per hour
Ditto	14 hours	Do.	0·3496	0·0001	Nil	{ 303 c.c. per hour

TABLE II.

Condition.	Time.	Temperature.	Weight of oxide.	Loss.
—	—	—	0·4190	—
Heated in a slow current of air	5 hours	100—105° C.	0·3949	0·0241
Ditto	14 hours	115° C.	0·3932	0·0017
Ditto	5 hours	110—120° C.	0·3932	Nil.
Ditto	5 hours	200—210° C.	0·3890	0·0042
Ditto	5 hours	210—230° C.	0·3878	0·0012

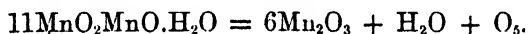
From Table I { 0.3779 gram lost 0.0283 gram, or 7.49 per cent.
 From Table II 0.4190 „ „ gave 0.0333 „ H₂O or 8.81 per cent.
 „ „ lost 0.0312 „ „ or 7.45 per cent.

The loss calculated from the equation above in the conversion of 10MnO₂.2MnO.6 $\frac{1}{2}$ H₂O into 11MnO₂.MnO.H₂O is 7.59 per cent.

II. In the difference in the relation of the manganese monoxide to available oxygen in the original oxide, and the oxide when heated to 200° C.

In the first case the percentage of oxygen to the monoxide is $\frac{14.06}{73.37} \times 100 = 18.65$ per cent., in the second case $\frac{16.79}{81.48} \times 100 = 20.61$ per cent.

III. By the loss on ignition in oxygen and the conversion of monohydrated higher oxide into the black sesquioxide* (following the change first pointed out by Dittmar (*Chem. Soc. J.*, 1865, 294). The reaction would be as follows:—



The theoretical loss in this case is 9.38 per cent. The following results (p. 587) were obtained by igniting the substance (dried at 200° C.) until the weight was constant:—

		Time.	Temp.	Weight of oxide.	Loss.	Loss per cent.
A {	Ignited in a current of oxygen	4 hrs.	Redness	0.3496 grm.	0.0331	9.47
B {						
C {						
	Ditto.....	Do.	Do.	0.2928 „	0.0280	9.56
	Ditto.....	Do.	Do.	0.3472 „	0.0326	9.41

A and B were samples prepared from Görgen's oxide described above. C a sample from another specimen of the oxide prepared by the same process. The fact of the absorption of oxygen simulta-

* Experiment showed that the conversion of the sesquioxide into the red oxide by ignition in nitrogen requires a far higher temperature than that needed for the conversion of the higher oxides into the sesquioxide, or the latter into the monoxide. At temperatures at which hard glass tubing (as used for organic analysis) softened, the sesquioxide remained unchanged in pure nitrogen, whether moist or dried by passing through the apparatus described above. In fact, the red oxide, a sample of which was prepared by igniting in a crucible the manganese monoxide residue obtained in the course of analysis (and therefore containing no alkali), was heated in a stream of oxygen at a low red heat; it changed from a reddish-brown to a black colour, and in about 24 hours was converted into the sesquioxide (gain per cent. : found, 9.33; theory, 9.49).

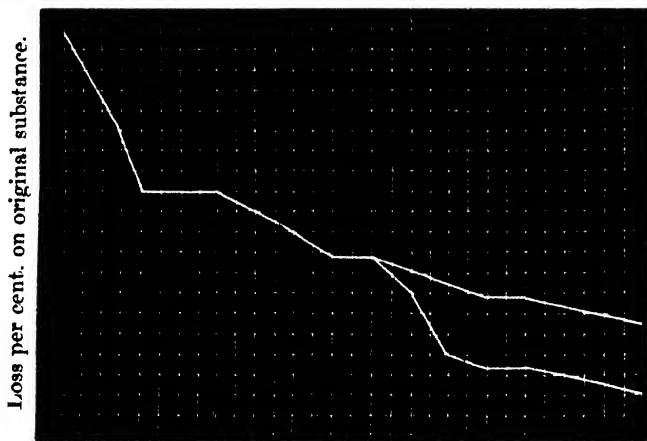
Continuous Series in Air.

Condition.	Time.	Temperature.	Weight of oxide.	Loss.	H ₂ O collected.	D.*	Remarks.
Heated in a slow current of air	—	—	0.4790 gram.	—	—	—	
Ditto	2 hours	59—63°	0.4666 "	0.0124	0.0120	-4	} 5MnO ₂ .MnO.2H ₂ O
Ditto	2 "	63—70	0.4601 "	0.0065	0.0065	-5	
Ditto	2 "	70—80	0.4601 "	Nil	Nil	Nil	
Ditto	2 "	87—90	0.4601 "	Nil	Nil	Nil	
Ditto	2 "	100—103	0.4582 "	0.0019	0.0023	+4	2(5MnO ₂ .MnO)3H ₂ O
Ditto	1½ "	110—115	0.4553 "	0.0029	0.0031	+2	
Ditto	3 "	119—121	0.4530 "	0.0023	0.0031	+7	
Ditto	1½ "	129—130	0.4530 "	Nil	Nil	Nil	
Ditto	1½ "	139—140	0.4520 "	0.0010	0.0036	+26	2(11MnO ₂ .MnO)3H ₂ O
Ditto	3 "	147—149	0.4506 "	0.0014	0.0076	+62	
Ditto	2 "	160	0.4490 "	0.0016	0.0014	-2	
Ditto	2 "	169—170	0.4489 "	(0.0006) nil	(0.0002) nil	Nil	
Ditto	2 "	189—190	0.4477 "	0.0012	0.0009	-3	11MnO ₂ .MnO.H ₂ O Mn ₂ O ₃ MnO
Ditto	2 "	190	0.4470 "	0.0007	0.0009	+2	
Ditto	2 "	202	0.4460 "	0.0010	0.0009	Nil	
Ditto	2 "	202	0.4460 "	Nil	Nil	Nil	
Oxygen	2 "	Low redness	0.4040 "	0.0420	0.0070	-350	
Ditto	2 "	" "	0.4040 "	Nil	Nil	Nil	
Ditto	2 "	Bright redness	0.3626 "	0.0414	—	—	
Hydrogen	2 "						

* D = difference in decimilligrams.

neously with, but probably not dependent upon, the giving off of water, seems to be established by the above results; and, as further preliminary experiments pointed to the formation of stable hydrates, which could be kept for several hours without giving off water or absorbing oxygen, a series of experiments were made with these objects (i) to find these hydrates and the limits of temperature between which they remain stable; (ii) to find the lowest temperature at which the absorption of oxygen begins in air. For these experiments the thermometer was enclosed in a piece of combustion tubing in order to mark more exactly the temperature in which the oxide was placed. Enclosed in the air-bath was an automatic oil and mercury regulator to keep the pressure of the gas constant; by its aid the temperature could be kept for many hours to within half a degree of that required. The changes which take place in the series p. 587 may be graphically illustrated by a curve in which the ordinates represent the percentage loss on the original substance, and the abscissæ the degree Centigrade; the difference between the upper curve deduced from the loss of the oxide, and the lower deduced from the gain in the drying tube is clearly perceptible.

CURVE I. DEGREES CENTIGRADE.



Remarks on the Table.

I. The temperatures at which stable hydrates seemed to be formed were 60—100° C., 120—130° C., 160—170° C., and 200° C.

II. The absorption begins at 140° C. and ends at 160° C., where there is a well-marked difference between the loss of the oxide and the water collected in the drying tube. Further analyses by the process described above were made in order to investigate the composition of the hydrates.

Analysis of the Oxide when Air-dried to 60—100° C.

	Values obtained.	Mean.	Calculated for (5MnO ₂ .MnO)2H ₂ O.
Manganese monoxide..	78·73	78·73	78·58
Oxygen	14·59 (a), 14·6 (a)	14·60	14·77
Water	6·57	6·57	6·65
		99·90	100·00

Analysis of the Oxide when Air-dried to 120° C.

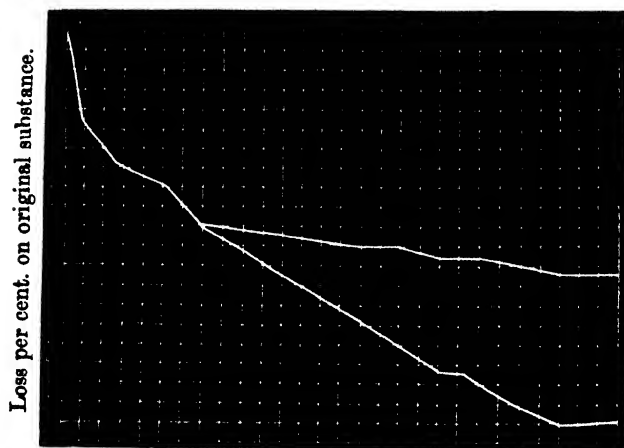
	Values obtained.	Mean.	Calculated for 2(5MnO ₂ .MnO)3H ₂ O.
Manganese monoxide..	80·27, 80·25	80·26	80·38
Oxygen	14·90 (a)	14·90	15·11
Water	4·56, 4·74	4·60	4·51
		99·76	100·00

Analysis of the Oxide when Air-dried at 160—170° C.

		Calculated for 2(11MnO ₂ .MnO)3H ₂ O.
Manganese monoxide	80·87	80·75
Oxygen (by difference)	16·63	16·69
Water	2·50	2·56
	100·00	100·00

The experiments were repeated with oxygen substituted for air: before the drying tube was weighed the oxygen was displaced by air, dried by passing slowly through a wash-bottle containing strong sulphuric acid.

CURVE II. DEGREES CENTIGRADE.

*Continuous Series in Oxygen.*

Condition.	Time.	Temperature.	Weight of oxide.	Loss.	H ₂ O coll.	D.	Remarks.
Heated in a slow current of oxygen, the rate of flow being about 20—23 bubbles per minute	—	—	0·4851 grm	—	—	—	
	2 hrs.	60° C.	0·4716 "	0·0135	0·3135	Nil	
	2 "	70	0·4680 "	0·0036	0·0036	Nil	
	2 "	80	0·4653 "	0·0027	0·0025	-2	
	2 "	90	0·4611 "	0·0042	0·0046	4	
	2 "	100	0·4587 "	0·0024	0·0030	6	
	2 "	110	0·4561 "	0·0026	0·0036	10	
	2 "	120	0·4538 "	0·0023	0·0050	27	
	2 "	130	0·4538 "	Nil	0·0030	30	
	2 "	140	0·4535 "	0·0003	0·0021	18	
	2 "	149	0·4521 "	0·0014	0·0018	4	
	2 "	160	0·4521 "	Nil	(0·0003)	} Nil	
	2 "	170	0·4511 "	0·0010	0·0012		2
	2 "	180	0·4505 "	0·0006	0·0020	14	
	2 "	189	0·4505 "	Nil	Nil	Nil	
Ignition ..	1 hr.	{ Low redness	} 0·4086 "	0·0419	0·0080	-339	
Ditto	1 "	{ Do.	} 0·4077 "	0·0009	Nil	-9	Mn ₂ O ₃
Ignition in hydrogen	1 "	{ Bright redness	} 0·3645 "	0·0432	—	—	
Ditto	2 hrs.	{ Do.	} 0·3645 "	Nil	—	Nil	MnO

Remarks on the above Table.

I. As should naturally be expected, the absorption of oxygen begins to take place at a lower temperature (about 90—100° C.) in oxygen than in air, the oxidation is more complete, the composition of substance obtained approximating more nearly to the dioxide, MnO₂.

II. The temperatures at which stable hydrates seem to be formed are 150—160° C. and 180—190° C., the oxide when heated to this latter temperature having the following composition:—

		Calculated for 23MnO ₂ .MnO ₂ H ₂ O.
Manganese monoxide....	80.91	80.82
Oxygen (by difference) ..	17.32	17.47
Water	1.77	1.71
	<hr/> 100.00	<hr/> 100.00

The numbers obtained by analysis agree with the formula, 23MnO₂.MnO₂H₂O, formed from the original oxide according to the following equation:—



Inasmuch as it has been suggested that pure manganese dioxide, MnO₂, loses oxygen at 160—200° C., while the experiments described in this paper point to an absorption of oxygen at a somewhat lower temperature, it is probable that these changes between 160—200° C. counterbalance one another. The oxide, so far as regards the oxygen, is within these limits of temperature in a state of equilibrium. Experiments were made to ascertain whether the pure dioxide was formed under the most favourable conditions: (i) the oxide was heated at that temperature at which it showed the greatest tendency to absorb oxygen (130—140° C.); (ii) the time of each experiment was lengthened.

Analysis of the Oxide heated in Oxygen for several hours to 133° C. till the Weight was Constant.

Manganese monoxide	80.76, 80.52	80.64
Oxygen	17.10 (a)	17.10
Water	2.17, 2.21	2.19
		<hr/> 99.93

The relation of the manganese monoxide to the oxygen in this case is $\frac{17.10}{80.64} \times 100 = 21.3$, which is approximately the same as that above, 23MnO₂.MnO = 21.44 per cent.; the alteration in the conditions does not affect the results. In no case, at least of many samples which were analysed, was the pure dioxide, MnO₂, obtained.

Conclusions.

I. The higher oxide prepared by the action of chlorine for a limited

time on the acetate of manganese, is a hydrated manganese manganite, $\text{MnO}, 5\text{MnO}_2 = \text{Mn}_6\text{O}_{11}$.

II. This oxide when heated in a current of air absorbs oxygen, and is converted into a hydrated oxide, $\text{MnO}, 11\text{MnO}_2 \cdot \text{H}_2\text{O}$; the lowest temperature at which the commencement of this change was observed was 140°C .

III. When heated in oxygen there is a greater absorption of oxygen, an oxide of the formula $23\text{MnO}_2 \cdot \text{MnO} \cdot 2\text{H}_2\text{O}$ being formed; in no case, even under the most favourable conditions, was the dioxide, MnO_2 , formed. The lowest temperature at which the commencement of this change was observed was 100°C .

IV. The manganese manganite forms hydrates, stable for many hours within certain limits of temperature, a dihydrate, $\text{MnO}, 5\text{MnO}_2 \cdot 2\text{H}_2\text{O}$, and sesquihydrate, $2(\text{MnO}, 5\text{MnO}_2) \cdot 3\text{H}_2\text{O}$.*

I wish to express my best thanks to Mr. Vernon Harcourt, not only for the preparation of the oxide on which the experiments described in this paper were made, but also for most valuable suggestions and assistance during the course of the investigation.

LI.—On Pentathionic Acid.

By T. TAKAMATSU and WATSON SMITH, Demonstrator and Assistant Lecturer on Chemistry in the Owens College.

THE doubts which are entertained respecting the very existence of pentathionic acid led us, at Dr. Roscoe's suggestion, to undertake the investigation of which we now give the results, prefacing the account however with a brief introductory sketch of such previous observations as enter most into the controversy and bear upon the salient points of the question.

Some years ago Kessler (*Pogg. Ann.*, **74**, 249) investigated the subject, and sought to confirm the existence of pentathionic acid in the solution obtained by Wackenroder's (*Ann. Chim. Phys.* [3], **20**, 144) original method, by means of a reaction with mercuric cyanide, which yields with this solution a reaction differing from that observed in the case of the other thionic acids. This difference consists in that, whilst with both tetrathionic and pentathionic acids free sulphur is liberated,

* The question whether manganese dioxide forms manganites with the oxides of metals was discussed at some length before the Newcastle Chemical Society (*Chem. News*, **41**, 180) while the present investigation was being carried on.

with pentathionic acid twice as much of this element is set free as with tetrathionic acid. These reactions are illustrated as follows:—

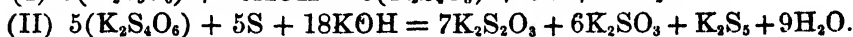
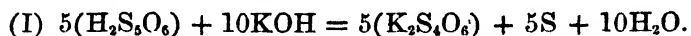
- (1) $\text{H}_2\text{S}_2\text{O}_3 + \text{Hg}(\text{CN})_2 + \text{H}_2\text{O} = \text{H}_2\text{SO}_4 + \text{HgS} + 2\text{HCN}.$
- (2) $\text{H}_2\text{S}_3\text{O}_6 + \text{Hg}(\text{CN})_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{HgS} + 2\text{HCN}.$
- (3) $\text{H}_2\text{S}_4\text{O}_6 + \text{Hg}(\text{CN})_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{HgS} + 2\text{HCN} + \text{S}.$
- * (4) $\text{H}_2\text{S}_5\text{O}_6 + \text{Hg}(\text{CN})_2 + 2\text{H}_2\text{O} = 2\text{H}_2\text{SO}_4 + \text{HgS} + 2\text{HCN} + 2\text{S}.$

Thus, mercuric cyanide decomposes all these polythionic acids in a manner very convenient for quantitative analytical determination. As a mean of many careful experiments, Kessler determined the quantities of sulphur, (*a*) in the sulphuric acid, (*b*) in the mercuric sulphide, and (*c*) the free sulphur formed. He thus obtained for the ratios *a* : *b* : *c* in the case of Wackenroder's solution, obtained by the action of SO_2 and H_2S in presence of water, the experimental numbers 2·01 : 1 : 2·08. Now had the acid under examination been tetrathionic acid, the relationship must have been *a* : *b* : *c* = 2 : 1 : 1, and this latter fact was practically demonstrated by similarly conducted analyses of the potassium tetrathionate.

In the course of last year (*Ann. Chem. Pharm.*, 199 [1], 107) Spring made a critical investigation of the subject. Obtaining a solution of the acid by Wackenroder's method, he concentrated it by evaporation, and obtained a potassium salt, by first treating the ethereal solution of the acid obtained by shaking with ether, with pure alcohol, and then adding a dilute solution of potassium carbonate and shaking. The salt obtained dissolved in water according to Spring without leaving behind it the least residue of sulphur. It was deposited in small thin needles, and he states that the solution of these gave the reactions which are attributed to pentathionic acid. Spring's analyses of this salt undoubtedly prove it to be a tetrathionate. Hence Spring looks upon the existence of pentathionic acid as a myth, and endeavours to show in a variety of ways that all former observers have been mistaken, as they have had after all nothing but tetrathionic acid in their hands.

Next come experiments by Stingl and Morawski (*J. pr. Chem.* [2], 20, 76—105), who give both qualitative and quantitative results, showing that an acid containing more sulphur than tetrathionic acid, really exists in the Wackenroder solution, and they draw attention to a qualitative reaction, by which pentathionic acid is clearly distinguished from any other of the thionic acids. They show, namely, that solutions of the alkaline and earthy hydrates immediately decompose this acid, with separation of sulphur. Alkaline carbonates effect the same decomposition, and even earthy carbonates slowly and on standing, the simple fact appearing to be that whilst the free acid is

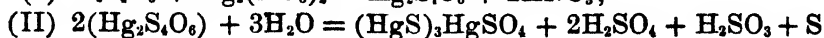
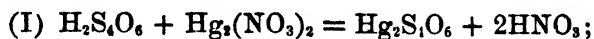
stable its salts are the very reverse. The precipitate of sulphur with the alkaline hydrates Stingl and Morawski found to be redissolved on boiling, with formation of polysulphides, easily detected with a drop of alkaline lead solution. The precipitated sulphur was also redissolved on standing, a portion being, according to the authors, first converted into alkaline sulphides, which dissolve more sulphur, with formation of thiosulphates. They represent the reactions which occur on treatment with potash, as follows:—



Stingl and Morawski further point out that free pentathionic acid is oxidised by potassium permanganate solution to trithionic acid without separation of a brown precipitate, and without addition of sulphuric acid. Tetrathionic acid is in like manner oxidised direct to trithionic acid, without precipitation. But setting out again with trithionic acid, even in presence of sulphuric acid, the first drop of permanganate causes precipitation at the ordinary temperatures, of a fine brown powder, of a manganese oxide. If now the solution obtained by Wackenroder's method, be titrated with permanganate till the brown colour appears, a considerably larger quantity of oxygen is needed, than would have been the case if a corresponding amount of tetrathionic acid had been present in solution. They also showed that with great excess of sulphuric acid and heating the solution, complete oxidation to SO_3 was effected, $H_2S_5O_6 + K_4Mn_2O_{10} + H_2SO_4 = 2K_2SO_4 + 4MnSO_4 + 2H_2O$. The authors assert that the pentathionic acid solution decomposed by alkaline hydrates or carbonates as already mentioned, yields tetrathionic acid as a product, and add that this is proved by the fact that permanganate solution oxidises the filtered liquid in the cold. If a pentathionic acid solution be treated with calcium carbonate, calcium tetrathionate is said by them to be formed; on standing, trithionate results, and finally calcium sulphate and sulphur. Stingl and Morawski also observed that on attempting to titrate a pentathionic acid solution with potassium permanganate (the acid obtained by Wackenroder's method, and cleared of finely divided sulphur, by addition of $CaCl_2$ solution and filtering), too low results were obtained owing to separation of sulphur during the process of titration. Oxidation with $KClO_3$ and HCl , and estimation of the sulphuric acid formed, with barium chloride solution confirmed this. From these experiments the above-named authors give an affirmative answer to the question of the existence of pentathionic acid.

Very recently Kessler (*Ann. Chem. Pharm.*, **200** [1 and 2], 256) combated Spring's views and conclusions, and Spring (*ibid.*, **199**, 118; also *ibid.*, **201**) in reply, asserts that the solution alleged to con-

tain pentathionic acid in fact consists of a solution of tetrathionic acid, together with some hyposulphurous acid, and that on removal of the latter acid, the solution gives with mercurous nitrate the following reactions:—



from which Spring concludes that only tetrathionic acid remains in the solution. He also asserts that this solution has the power of decolorising indigo, and concludes that the so-called and so-obtained pentathionic acid is nothing more than a mixture of tetrathionic and hyposulphurous (H_2SO_2) acids, the latter acid, as Schützenberger has shown, being the only sulphur acid known which possesses the power of decolorising indigo.

We commenced our own experiments by the preparation according to Wackenroder's method of a quantity of the so-called pentathionic acid solution, for the purpose of repeating the quantitative experiments of Stingl and Morawski and Kessler on the one hand, and of Spring on the other.

Hydrogen sulphide was passed into a saturated solution of sulphurous acid, until the smell of sulphur dioxide was no longer perceptible. The precipitated sulphur obstinately passing through the filter even after shaking the liquid with freshly precipitated metallic copper, a small quantity of freshly precipitated barium carbonate was added, and on immediate filtration a perfectly clear fluid was obtained. Though at first quite limpid, however, this filtrate gradually became turbid, from a slight decomposition of the sulphur compound formed. A current of CO_2 was then immediately passed through the solution in order to remove any sulphuretted hydrogen present in excess, the presence of which would account for the decomposition of the sulphur acid. The solution was then warmed and again filtered from the separated sulphur. This time the filtrate remained quite clear, and continued so permanently. The small quantity of barium present was removed by exactly sufficient dilute sulphuric acid, and the acid liquid concentrated by evaporation to about one-third of its bulk. The object of the first experiment, following Stingl and Morawski, was to determine the amount of sulphur in a known volume of the acid. This was calculated from the amount of oxygen expended by potassium permanganate in converting the thionic acid into sulphuric acid. It was further necessary to ascertain whether this amount of sulphur corresponds to the amount which should be found, if this acid really be pentathionic acid or any other, by comparing the total sulphur independently estimated in a similar volume of the acid solution. For this purpose 10 c.c. of the acid solution were taken and acidified with

an excess of dilute sulphuric acid, and then titrated with the permanganate solution, of which each c.c. = 0.00164 gram of available oxygen. If the operation were conducted in the cold, a brown precipitate was formed, which rendered it impossible to observe the end of the reaction. It was therefore necessary to heat the acidified solution and conduct the process exactly as described by Stingl and Morawski.

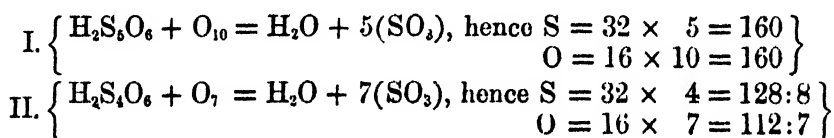
10 c.c. of the acid solution required 120.4 c.c. permanganate solution.

10 c.c.	"	"	"	120.0	"	"	"
10 c.c.	"	"	"	120.0	"	"	"

Mean..... 120.1 "

Hence $120.1 \times 0.00164 = 0.19696$ gram of oxygen was needed for the complete oxidation to sulphuric acid. Now if this solution contained pentathionic acid ($\text{H}_2\text{S}_5\text{O}_6$), the amount of sulphur corresponding or equivalent to the oxygen required for the complete oxidation, would be also 0.19696 gram, whereas, if the solution merely contained tetrathionic acid ($\text{H}_2\text{S}_4\text{O}_6$), the amount of sulphur would be $0.19696 \times \frac{8}{7} = 0.2251$ gram. The reason for this we will now show.

A molecule of tetrathionic acid requires *less* oxygen for its complete oxidation to sulphuric acid than a molecule of pentathionic acid does. Consequently, for the same amount of oxygen actually required, the number of molecules present in the case of tetrathionic acid must be greater, and contain a larger amount of sulphur than if pentathionic acid alone were present. The ratio of the weight of oxygen to that of sulphur required for complete oxidation, is that of equality in the case of pentathionic acid, whilst it is as 7:8 in the case of tetrathionic acid. This is evident from a consideration of the following equations:—



The total amount of sulphur actually present in the acid solution, was determined by previously oxidising the solution with potassium chlorate and hydrochloric acid, and then precipitating as barium sulphate.

From 10 c.c. of the acid solution—

	I.	II.
BaSO ₄ obtained	1·6188 gram.	1·6184 gram.
Corresponding to S	0·2223 „	0·2222 „
S deduced from oxygen, required for H ₂ S ₅ O ₆	By titration with permanganate	0·19696
S deduced from oxygen, required for H ₂ S ₄ O ₆		0·2251

But Stingl and Morawski observed that some sulphur is separated during titration, and hence too low a number is obtained. Stingl and Morawski state that this separation of sulphur is due to a decomposition of the tetra- and tri-thionic acids formed, in titrating with permanganate in presence of much sulphuric acid. We found that the end of the reaction was almost impossible to hit, owing to the dark colour acquired by the solution, and we cannot therefore attach much importance to the above numbers obtained, or to the process.

A determination was now made by Kessler's method, by estimating the amounts of sulphuric acid, mercuric sulphide, and free sulphur obtained by the action of mercuric cyanide on the freshly prepared acid solution obtained by Wackenroder's method. For this purpose 10 c.c. of the solution were taken and boiled with an excess of mercuric cyanide till the yellow precipitate, which was at first formed, became black. The mercuric sulphide containing free sulphur was then thrown on to a weighed filter, dried at 100°, and weighed. The whole was then treated with strong nitric acid, with addition of potassium chlorate to oxidise the sulphur completely to sulphuric acid, which was estimated as barium sulphate. From the latter the total sulphur was calculated, and this deducted from the contents of the weighed filter dried at 100° (mentioned above) gave the mercury, from which the sulphur as sulphide was at once deduced, leaving that which was in the free state.

Thus, then, the following results were obtained:—

	Mol. weight.	Mol. ratios.
H ₂ SO ₄ = 0·3929 gram ÷ 98		= 0·00390 : 2
HgS = 0·4549 „ ÷ 232		= 0·00196 : 1
S = 0·1227 „ ÷ 32		= 0·00383 : 1·95
Amount of sulphur in the H ₂ SO ₄ formed		= 0·1283
„ „ HgS „		= 0·0627
Free sulphur		= 0·1227
Total sulphur		= 0·3137

The total sulphur was estimated independently by oxidising the acid solution with potassium chlorate and hydrochloric acid. Thus from 10 c.c. of the solution 2·3383 grams of BaSO₄ were obtained, which

gives 0.3211 gram of total sulphur as against the number 0.3137 gram deduced from the data yielded in the former experiment by Kessler's method. This experiment indicates that the solution contained pentathionic acid, for in the case of tetrathionic acid the ratios of H_2SO_4 , HgS , and S ought to be 2 : 1 : 1, whereas we, like Kessler, obtain the relation 2 : 1 : 2 practically.

Decomposition of the Wackenroder Solution by Alkaline and Earthy Carbonates and Hydrates.

Stingl and Morawski observed, as already stated, that by the action of alkaline and earthy carbonates on the pentathionic acid solution, thiosulphuric acid is formed and sulphur deposited. But the most characteristic reaction for pentathionic acid is the one with caustic alkalis and consequent precipitation of sulphur, upon which stress was laid by Stingl and Morawski. Lime-water has a similar effect, and we find that the addition of ammonia solution even causes precipitation after a few seconds. To a solution of the acid, magnesia was added in fine powder. The magnesia dissolved, when the acid was in excess, to a clear solution, remaining clear for a considerable time. On adding excess of magnesia, however, and then attempting to redissolve by adding excess of the acid solution, the magnesia was dissolved, but a white precipitate of sulphur remained. Spring appears to doubt that the precipitate formed in such a case as this does entirely consist of sulphur. This point we have frequently proved by collecting the precipitates formed, washing, drying, and carefully heating in the flame, when the residue burns with a blue flame, smells of SO_2 , and leaves no residue.

Now in all cases the precipitate of sulphur formed by the action of caustic alkaline solutions in excess on the acid Wackenroder solution, after standing for some hours completely redissolves. If the precipitate with solution be boiled, the former is almost immediately redissolved, and sulphides or polysulphides are formed, and then a black precipitate is produced with a few drops of an alkaline lead solution. The solution in which the sulphur has redissolved *on standing merely*, does not precipitate lead solution black. The two following experiments show that not only the excess of alkaline hydrate, but also the *decomposition products* of the pentathionic acid, play a part in the re-resolution of the sulphur:—

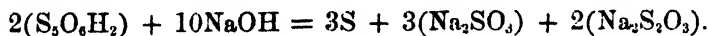
(I) On cautiously adding acid to the sodium hydrate solution containing the precipitated sulphur, till neutrality was attained, on standing, re-resolution of the sulphur does *not* take place.

(II) On letting the freshly precipitated solution stand till the sulphur has settled down (hastened by first shaking the liquid), and then

washing by decantation with water, till the finally decanted liquid was no longer alkaline to test-paper, when excess of caustic soda solution was added, solution of the sulphur did not occur after standing for three days. (If not washed thus, standing for 4—5 hours would have been sufficient for re-solution.)

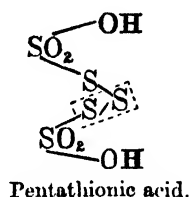
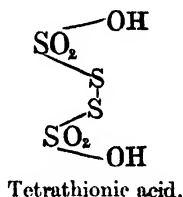
The filtrate from the precipitated sulphur contained thiosulphates, sulphites, but *no sulphides*. Likewise the clear solution, obtained on letting the alkaline solution turbid with sulphur stand, was found to contain no sulphides, only sulphites and thiosulphates appearing to be present. In this respect we differ from Stingl and Morawski, who state, in the equation they give (p. 593), that polysulphides are formed. It would also appear from their equation that in the turbid fluid (from precipitated sulphur) no sulphites are present, which is not true. This we proved by immediate filtration, and testing the clear filtrate for sulphites in the usual way. But we found in this latter case thiosulphates present as well as sulphites, whose joint presence at once indicates the impossibility of tetrathionic acid having been formed, the contrary of which Stingl and Morawski's equation would make apparent. The application of the fact by Stingl and Morawski, that potassium permanganate solution is decolorised without a precipitate and in the cold by the clear filtrate from the precipitated sulphur, to demonstrate the presence of tetrathionic acid in that solution, fails in its object, since the presence of thiosulphates would also account for this deoxidation and decolorisation.

The observations we have made show us that by the action of *aqueous solutions* of the alkaline hydrates a complete rupture of the pentathionic acid molecule may be regarded as taking place, free sulphur, sulphites, and thiosulphates being formed. We were thus led to the adoption of the following equation as illustrating the reaction most probably taking place:—



We at first thought that on re-solution of the sulphur after standing the following reaction occurs, $3\text{S} + 3(\text{Na}_2\text{SO}_3) = 3\text{Na}_2\text{S}_2\text{O}_3$, in which case no sulphites should remain. But sulphites do exist in the cleared solution: hence, as Stingl and Morawski remark, the sulphur is in all probability partly taken up to form sulphide by the excess of caustic soda, and almost simultaneously the sulphide takes up oxygen together with more sulphur, forming thiosulphates. Of the presence of sulphites we have had ample proof. We are perfectly aware of the fact that the reaction we have used for detecting thiosulphuric acid, viz., the action of dilute hydrochloric acid, causing simultaneous precipitation of sulphur and evolution of SO_2 , applies equally to the detection of trithionic acid, but it would be very difficult to under-

stand how trithionic acid could be formed under these circumstances, *i.e.*, simultaneously with sulphurous acid. A glance at the structural formula of pentathionic acid, which must belong to this acid (its existence being taken for granted), and the structural formula for its homologue, tetrathionic acid, being known to be—



will now show that our equation would appear to be the simplest and the most natural; also only bodies figure in it whose presence we have proved. In the above formula for pentathionic acid such a splitting off of sulphur also as is indicated by the dotted lines perfectly agrees with the meaning of our equation given above, and now it will be apparent too that if sulphites be formed in the reaction together with separation of sulphur, the formation of trithionic acid can hardly be considered possible. However the same formula shows that our view expressed in the equation proposed is most simply in accordance with the facts we observe, that pentathionic acid is split up by the action of caustic alkali into sulphur, thiosulphuric and sulphurous acid residues.

We now endeavoured to ascertain the conditions under which the finely divided precipitate of sulphur is so comparatively quickly redissolved, after precipitating the Wackenroder solution, with excess of sodium hydrate. For this purpose we took three test-tubes, and introduced into each about an equal amount of finely divided sulphur which had been precipitated from dilute yellow ammonium sulphide solution by addition of hydrochloric acid. Sodium hydrate solution was then added in equal volume to each tube, and in the first was placed a little sodium sulphite solution, in the second a little sodium thiosulphate, and in the third a mixture of these two salts. After standing for about two days, we found in the case of the tube containing the sulphite, complete solution had almost taken place. In the case of the thiosulphate, and of the mixture of thiosulphate and sulphite, however, less solution of the sulphur had been effected.

We find also on precipitating a pentathionic acid solution with an alkaline hydrate, if the precipitate of sulphur be large and be further coagulated by shaking, solution then takes place only after a considerably longer time than is required if the solution be diluted previous to decomposition and shaking be avoided, so that no coagulation

occurs. The more rapid solution appears then to ensue when the sulphur is in the finest possible state of molecular division. A mere milkiness or opalescence disappears in about the course of an hour.

With regard to Spring's statement, that the so-called pentathionic acid is nothing more than tetrathionic acid, all the reactions of which it gives, there is one point on which we speak with the most complete confidence, viz., that a solution of tetrathionic acid is not decomposed by alkaline hydrates in the slightest, and therefore it is clear that in Wackenroder's solution a different and much less stable thionic acid exists. But Spring goes further, and states that together with tetrathionic acid a small quantity of hyposulphurous acid is formed by Wackenroder's method, and that it is simply the mixture of these two acids which forms that apparently unstable body termed "pentathionic acid."

For the purpose of testing this question, a freshly prepared Wackenroder solution was carefully treated with an indigo solution of the faintest possible blue tinge. The acid solution was in large excess. This faint blue tinge *did not disappear* even after warming, and hence we conclude that no hyposulphurous acid was present. We next prepared a solution of hyposulphurous acid by the action of zinc-dust on sulphurous acid solution. A quantity of pure tetrathionic acid was also prepared by the action of iodine on barium thiosulphate, and subsequent removal of barium with sulphuric acid. A small quantity of the hyposulphurous acid was mixed with the tetrathionic acid solution. This solution not only readily decolorised indigo, but yielded not the slightest precipitate of sulphur with potassium and sodium hydrates. Even a strong hyposulphite solution does not precipitate sulphur when treated with KOH, &c., for the alkaline hyposulphites are stable and well defined salts. Both pentathionic and tetrathionic acids coincide in being decomposed by an alkaline sulphide or sulphhydrate solution, with precipitation of sulphur. This we have often verified, but an alkaline hydrate or carbonate, which combines with the former acid to form saline compounds rapidly decomposing, combines with the latter to form stable salts.

We next repeated Spring's analysis of the potassium tetrathionate, which he obtained by extracting the acid solution obtained by Wackenroder's reaction with ether, subsequently diluting with alcohol, and precipitating with potassium carbonate. Results were obtained precisely agreeing with the calculated numbers for potassium tetrathionate and with Spring's results generally (see p. 593). The potassium salt was as Spring described it, a snow-white crystalline salt, soluble in water without turbidity or residue. It gave all the reactions of tetrathionic acid, and certainly no precipitate of sulphur with sodium hydrate solution. Two determinations of potassium in

the salt gave results showing that the salt was a potassium tetrathionate:—

	Potassium per cent.
(I) 0.1475 gram of salt gave 0.085 gram of K_2SO_4 .	
From I	25.86
(II) 0.1170 gram of salt gave 0.068 gram of K_2SO_4 .	
From II	26.07
	<hr/>
Mean	25.97
Calculated for $K_2S_4O_8$	25.86
,, $K_2S_5O_8$	23.35

If the Wackenroder solution be shaken with ether, and the ethereal solution after dilution with alcohol be treated with potash, no precipitation of sulphur takes place, and the solution shows characteristic reactions of tetrathionic acid. On adding, however, a few drops of potash to the residual aqueous solution which had been shaken with the ether, an immediate precipitate of sulphur was thrown down.

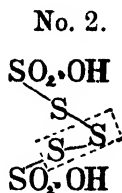
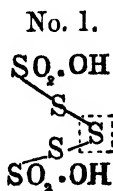
We at first thought that we had thus discovered in the ether a means of separating tetra- from penta-thionic acid, and that the Wackenroder solution must contain the latter acid mixed with a small proportion of the former, the tetrathionic acid being soluble, but the pentathionic acid insoluble in the ether. The following experiment showed us we were wrong. A quantity of Wackenroder solution was repeatedly shaken with fresh quantities of ether, with the object of gradually freeing it from tetrathionic acid, but this was found utterly impossible, since after between twenty and thirty agitations the ethereal extract gave unabated indications of the presence of tetrathionic (or pentathionic) acid with the silver nitrate reaction and with litmus-paper. We then suspected that it was merely the pentathionic acid which is slightly soluble in ether, which would account of course for a small quantity being continually taken up after each renewed agitation with ether.

The following experiments solved for us this apparent enigma, and demonstrated also the fallacy of Spring's conclusion, that he had obtained the potassium salt of the *actual acid* existing in, and by means of the treatment with ether or amyl alcohol, extracted from the Wackenroder solution, and remaining quite intact during the process, simply because the salt he obtained dissolved in water without leaving either residue or turbidity of sulphur. A small quantity of the Wackenroder solution was treated in a test-tube with strong alcohol, and thereafter the alcoholic solution, with ether. By this means a clear ether-alcoholic solution of the whole acid solution taken was obtained. On carefully adding a few drops of a pure caustic soda solution upon the surface of the liquid in the tube, an immediate tur-

bidity was produced just in the upper alkaline layer formed for the instant, evidently owing to separation of sulphur. On sinking through and mixing with the sub-natant ether-alcoholic fluid, the precipitate quickly disappeared again. On adding more caustic soda, a further precipitate appeared, soon disappearing on gentle agitation. It thus became clear to us that a separation of very finely divided sulphur *does* take place, on treating an ethereal pentathionic acid solution with alkalis, but without turbidity, because the finely divided sulphur is instantly dissolved by the ether. In the above experiment on adding excess of soda, at length a yellow ethereal layer was formed in the upper part of the solution, consisting of an ethereal solution of the sulphur, separated in an extremely finely divided condition. It would appear, then, that separation and solution of the sulphur became almost simultaneous processes.

From a further experiment it would appear that the sulphur thrown down in an aqueous solution by the action of alkalis, is precipitated in a physically coarser condition than in an ethereal solution. Some of the Wackenroder solution was mixed with a little potash, whereby a precipitate of sulphur was at once formed, excess of ether and alcohol were then added, but the sulphur was not nearly so quickly or easily dissolved as in the former case, in which the precipitation took place in the ether-alcohol solution.

We thus see why Spring obtained a potassium tetrathionate salt quite free from sulphur, in the manner he describes, for the sulphur, as soon as liberated from the pentathionic acid, was immediately dissolved and taken up by the ethereal alcohol solution. With regard, however, to a tetrathionate being formed in an ethereal or alcoholic-ethereal solution, and mixed sulphites and thiosulphates in an aqueous solution, we are brought to the conclusion that in the former case a feebler reaction ensues, and less sulphur is abstracted than in the latter case, where more sulphur being set free, a complete disruption of the pentathionic acid molecule takes place, the two cases being thus exemplified:—



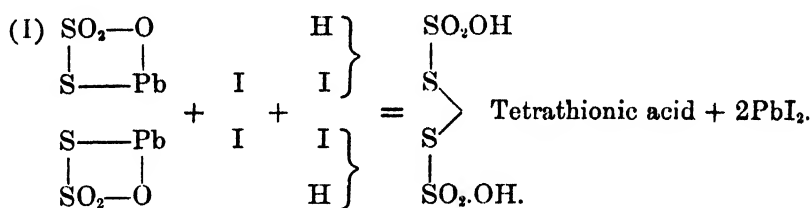
No. 1. Action of alkalis in ethereal or ether-alcohol solution.

No. 2. Action of alkalis in aqueous solution on the pentathionic acid molecule.

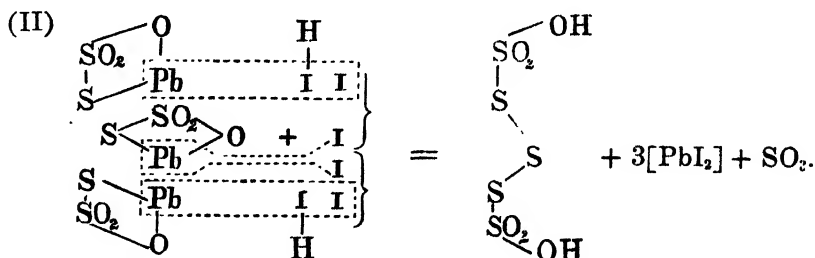
Synthesis of Tetrathionic and Pentathionic Acids from the same materials.

It now became evident to us that in order to throw clearer light upon the question of the absolute identity of this pentathionic acid, it would be necessary to attempt its synthesis, developing the acid according to a preconceived theoretical scheme, and if by the use in duly modified proportions of the same ingredients its tetrathionic homologue could be formed, of whose identity and constitution little doubt can exist, then it would appear that our grounds of argument as to both identity and constitution of pentathionic acid must be good.

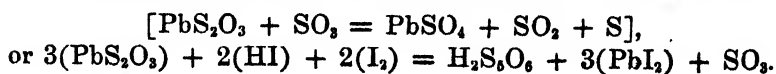
The following theoretical scheme was now drawn up by one of us (W.S.) as a possible means of satisfying the above-named requirements. It was proposed to endeavour firstly to synthesise tetrathionic acid by the action of a solution of iodine in hydriodic acid or potassium iodide, upon lead thiosulphate suspended in water, according to the following equation:—



And thereafter, to use a solution of iodine in hydriodic acid, as concentrated as possible, containing about the following proportions:— $2(\text{HI}) : 2(\text{I}_2)$.

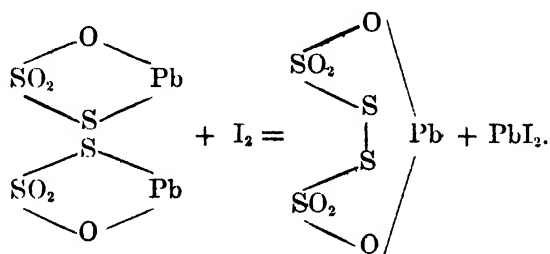


This SO_3 as SO_4H_2 would react on the excess of PbS_2O_3 , thus:—



Of course it would be quite possible, as may be anticipated, and as

we experimentally found, to prepare a lead tetrathionate by the action of a solution of iodine in spirits of wine, on lead thiosulphate, the reaction being the following :—



On treatment with dilute sulphuric acid or sulphuretted hydrogen, the free acid was obtained. I may just remark that the new method, of which the scheme has been just described, for obtaining and preparing pentathionic acid, is the most convenient and expeditious one in existence, for here the difficulty of dealing with finely divided sulphur, refusing to separate on the filter without the introduction of some foreign substance into the solution, is quite overcome.

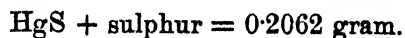
I. *Preparation of Tetrathionic Acid.*—Freshly prepared and washed lead thiosulphate, in the state of a thick mud, is mixed with some water, and shaken in a flask with solution of iodine in hydriodic acid, the solution being by no means a concentrated one, and the iodine solution being added little by little, with a thorough agitation after each addition, and finally stopping short of a final decomposition of the whole of the lead thiosulphate. After filtering, any lead in solution is removed by H_2S water, care being taken not to add too much. Sulphuric acid, with subsequent use of barium carbonate to remove its slight excess, is better. By this method, we found it often difficult to avoid the simultaneous formation of varying small quantities of pentathionic acid, whose presence we detected by the slight opalescence produced with caustic alkaline solutions, the well developed reaction with silver nitrate, &c. (*vide* Table, p. 608), showing that considerable quantities of tetrathionic acid were present. The most convenient method consists in using a potassium iodide solution of iodine, instead of the hydriodic acid solution. A concentrated solution may then be employed, with gentle warming to hasten the reaction. The final product is a pure and clear solution of potassium tetrathionate. Not a trace of pentathionic acid is formed.

II. *Preparation of Pentathionic Acid.*—Instead of the not very strong solution of iodine in hydriodic acid, a solution so concentrated should now be adopted that iodine is no longer taken up by it, but a residue thereof remains, and to the lead thiosulphate in the state of a thick mud, enough water is added to form with it a thin pasty mass. The

iodine solution is now added gradually with shaking, till on standing for a minute after a fresh addition and agitation, a faintly brown-coloured supernatant solution is observed. More water is now added, and the contents of the flask are then heated till the brown colour disappears, when fresh iodine solution is added, till at length a permanent excess remains, even on warming. Lead thiosulphate is now added in very small quantities, with agitation and warming, till the yellow tint of the supernatant fluid disappears, and a colourless solution remains, in which spangles of lead iodide are floating. The mixture after cooling, is now filtered, and hydrogen sulphide is freely passed through the filtrate to separate lead; as soon as this is effected, and the solution, after shaking, smells of H_2S , quite a concentrated and clear solution of pentathionic acid is obtained on again filtering. This solution, however, soon becomes turbid again, probably from contact with slight excess of H_2S left in the fluid. The latter is now removed by a stream of CO_2 , or air, and on filtering, evaporation, and again filtering, a concentrated solution is obtained, which should be allowed to stand one day or overnight, when a final filtration is generally needed. The clear liquid now obtained exhibits all the properties of a concentrated solution of pentathionic acid. The method has the several advantages of yielding a purer product than the others, and of doing so with great expedition, and little trouble. The great difficulty of Wackenroder's method, viz., the filtration from finely divided sulphur, is also avoided, for the solution in the case of our method leaves its finely divided sulphur behind with the lead sulphide, with the greatest ease. Dilute sulphuric acid may be used, with perhaps even more convenience for separating the lead than H_2S , the excess being afterwards removed by the addition of just enough BaCO_3 , followed by immediate filtration.

Analysis by Kessler's Method.

10 c.c. of the solution of the pentathionic acid prepared by the new method, were now treated with an excess of mercuric cyanide solution, till the precipitate, which was yellow, became quite black. The precipitate was thrown on to a weighed filter, washed, and dried at 100° , till the weight was constant.



The mixture was then dissolved in strong nitric acid, with addition of KClO_4 . After evaporating nearly to dryness, adding HCl , and again evaporating, the sulphuric acid in the diluted solution was determined as BaSO_4 .

Weight of BaSO_4 due to free sulphur and HgS = 0.4875 gram.
 This is equivalent to sulphur..... = 0.0669 „
 Hence weight of Hg (0.2062-0.0669)..... = 0.1383 „
 Equivalent to HgS = 0.1615 „
 And therefore free S = (0.2062-0.1615) = 0.0447 „

The filtrate from the HgS and free sulphur contained sulphuric acid, which was estimated. BaSO_4 due to sulphuric acid, = 0.3330 gram.

The relative weights of HgS , free S , and H_2SO_4 are then as follows:—

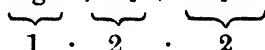
$$\text{HgS} = 0.1615; \text{S} = 0.0447; \text{H}_2\text{SO}_4 = 0.1400;$$

Dividing these numbers by their equivalent weights, the following numbers were obtained:—

$$\begin{array}{rclcl} \text{HgS} & = & 0.1615 & \div & 232 & = & 0.0007 \text{ or } 1. \\ \text{S} & & 0.0447 & \div & 32 & = & 0.0014 \text{ or } 2. \\ \text{H}_2\text{SO}_4 & = & 0.1400 & \div & 98 & = & 0.0014 \text{ or } 2. \end{array}$$



These ratios 1 : 2 : 2 exactly coincide with Kessler's equation,
 $\text{H}_2\text{S}_5\text{O}_6 + \text{Hg}(\text{CN})_2 + 2\text{H}_2\text{O} = \text{HgS} + \text{S}_2 + 2\text{H}_2\text{SO}_4 + 2\text{HCN}.$



With a fresh pentathionic acid solution not so carefully prepared and probably containing some tetrathionic acid, the following numbers were obtained:—

$$\begin{array}{rclcl} \text{HgS} & = & 0.2068 & \div & 232 & = & 0.00089 : 1 \\ \text{S} & & 0.0466 & \div & 32 & = & 0.00146 : 1.64 \\ \text{H}_2\text{SO}_4 & = & 0.1739 & \div & 98 & = & 0.00177 : 2 \end{array}$$

We have reason to believe that under given conditions the pentathionates can also be prepared, and we hope before long to lay the results of our experiments in this direction before the Society. The following table of the most characteristic reactions of the thionic acids may prove useful:—

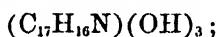
Reactions to distinguish Tetra- and Penta-thionic Acids from each other, and from the other Thionic Acids.

Reagents.	Dithionic acid, $\text{H}_2\text{S}_2\text{O}_6$.	Trithionic acid, $\text{H}_2\text{S}_3\text{O}_6$.	Tetrathionic acid, $\text{H}_2\text{S}_4\text{O}_6$.	Pentathionic acid, $\text{H}_2\text{S}_5\text{O}_6$.
Caustic potash	No precipitate	No precipitate	No precipitate	Immediate precipitate of sulphur, redissolving gradually on standing, if not in much excess and coagulated. No action.
Dilute hydrochloric acid.	No action	Evolution of SO_2 , and precipitate of S.	Yellow precipitate, gradually darkening.	At first yellow precipitate, turning white with excess of reagent on standing.
Mercurous nitrate	No precipitate	Immediate black precipitate, becoming white on standing.	Yellow precipitate, soon turning black, and also on adding ammonia.	Yellow precipitate, gradually darkening; black on adding ammonia.
Silver nitrate	No precipitate	Yellow precipitate, soon becoming black.	No dark or brown coloration, even on standing, <i>unless warmed</i> .	Almost immediate brown coloration, becoming black on warming.
Ammoniacal silver nitrate.	—	No brown coloration, even on standing. On warming, Ag_2S formed.	At first yellow precipitate; turns black on warming, with evolution of HCN .	At first yellow precipitate, gradually turning black on heating, with evolution of HCN .
Mercuric cyanide	No precipitate	—	On warming, white precipitate.	On warming, whitish yellow precipitate.
Mercuric chloride	No precipitate	Yellow precipitate, becoming white with excess of reagent.	White precipitate of sulphur.	White precipitate of sulphur.
Potassium sulphhydrate solution.	—	—	Decolorised, without addition of dilute H_2SO_4 .	Decolorised, without addition of dilute H_2SO_4 .
Dilute solution of potassium permanganate.	One drop, immediate brown precipitate.	One drop, immediate brown precipitate, even in presence of dilute SO_4H_2 .		

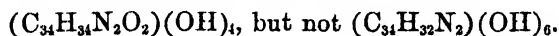
LI.—On the Action of Benzoyl Chloride on Morphine.

By C. R. ALDER WRIGHT, D.Sc. (Lond.), Lecturer on Chemistry, and
E. H. RENNIE, M.A. (Sydney), B.Sc. (Lond.), Demonstrator of
Chemistry in St. Mary's Hospital Medical School.

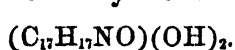
IN the course of a series of five papers "On the Action of Organic Acids and their Anhydrides on the Natural Alkaloids" (this Journal, 1874, p. 1031; 1875, pp. 15, 312, and 689; and 1876, vol. 1, p. 652), by one of us and Mr. G. H. Beckett, it was shown, *inter alia*, that when an organic acid acts on morphine one-third of the oxygen present is affected in such a way that the hydrogen originally indirectly linked by that oxygen to the rest of the structure (*i.e.*, existent as hydroxyl), becomes replaced by the acid radicle of the organic acid employed, giving rise to a new alkaloid of wholly basic character if the acid were mono-basic, *e.g.*, benzoic or acetic, and of mixed character, *i.e.*, partially basic, partially acid like glycocine (amido-acetic acid), if the acid were dibasic, *e.g.*, succinic or camphoric acid. On the other hand, when an organic anhydride, such as acetic benzoic or butyric anhydride, acts on morphine, twice, but not more than twice, the amount of hydrogen is replaced by the acid radicle that is replaced when the free acid is used; and from these and other circumstances the conclusion was drawn that for every 14 parts of nitrogen in morphine 2 parts of hydrogen exist as hydroxyl, and 17 in some other form of combination; whilst 32 parts of oxygen exist as hydroxyl, and the remaining 16 in some other form of combination. In other words, viewing morphine as indicated by the symbols, $C_{17}H_{19}NO_3$ (empirical formula), this formula may be written: $(C_{17}H_{17}NO)(OH)_2$, but not—



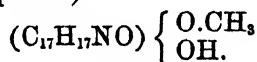
or if morphine be regarded as indicated by the double of the empirical formula (as a prolonged study of its derivatives has led one of us to believe to be the case), the formula may be written—



A further corroboration of the hydroxylic character of two-thirds but not of the whole of the oxygen in morphine is derived from the action of acids and anhydrides on codeine, which has been shown in former researches by one of us (in part conjointly with the late A. Matthiessen), to be a methylic ether of morphine, bearing to it the relation indicated by the formulæ (empirical)—



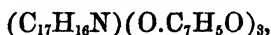
Morphine.



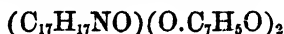
Codeine.

the hydroxylic hydrogen which is replaced by methyl being that which is presumably of a phenolic character, enabling the morphine to strike a blue tint with ferric salts: if the codeine be indicated by a formula in which only one-third of the oxygen is hydroxylic, evidently if an organic acid replace the hydrogen of that hydroxyl there is none left for an organic anhydride to replace further; so that the codeine, unlike morphine, should yield the same substitution product with an organic anhydride, as with the corresponding acid, which was shown to be the case in the above quoted series of papers.

A few months ago, however, a paper appeared by K. Polstorff (*Ber.*, 1880, 98), in which the author stated that by heating anhydrous morphine with twice its weight of benzoyl chloride to 100–110° in sealed tubes, for some hours, a tribenzoylated morphine,



was obtained, by dissolving the contents of the tube in a large bulk of hot water, precipitating by ammonia, and crystallising from alcohol. The evidence given of the substance being a tribenzoylated derivative, however, was absolutely *nil*! On analysis numbers were obtained which on the whole agree better with the formula—



(i.e., with the dibenzoylated base) than with the tribenzoylated derivative, taking the C_{17} or empirical formula for morphine for simplicity sake.

	Found by K. Polstorff.			Calculated.	
				For Dibenzoyl Morphine.	For Tribenzoyl Morphine.
Carbon ..	76.09	76.12	76.26	75.46	76.38
Hydrogen	5.84	5.75	5.83	5.47	5.19
Nitrogen	2.89	2.70		2.84	2.35

Notwithstanding, however, that the hydrogen and nitrogen determinations as far as they go tend to negative the idea of the substance being the tribenzoylated derivative, Herr Polstorff appears to consider that the excess of carbon found is indicative of that being the case, although a slight excess of carbon apparently found in the combustion of a nitrogenous substance (from oxides of nitrogen being absorbed by the potash) is no uncommon phenomenon; to check this conclusion, however, he made absolutely no determinations of the molecular weight of the substance, either by dissolving in dilute warm hydrochloric acid (in which he states it is slightly soluble, separating as an amorphous mass on cooling—doubtless of hydrochloride, that being the precise character of dibenzoyl morphine hydrochloride), and precipitating as platinochloride, aurochloride, &c., or by saponifying with alcoholic potash and determining the amount of benzoic acid formed.

Notwithstanding that Herr Polstorff's paper shows self-evidently that the data on which he founded his conclusions were insufficient, we have thought it right to repeat his experiments in order to see if it actually is the case that benzoyl chloride will replace a hydroxylic hydrogen in morphine on which the prolonged action of benzoic anhydride has no effect at all; with, as we expected, wholly negative results; *i.e.*, the product invariably contains two and not more than two benzoyl groups for every nitrogen present, or is the *di*- and not the *tri*-benzoylated base.

Commercially pure benzoyl chloride was redistilled to separate dissolved HCl gas and other impurities, and the fraction boiling at 190—200° collected and used; on decomposition by water this yielded pure benzoic acid.

Morphine dried at 100° was heated in a sealed tube with twice its weight of the chloride in one case for six hours, in another for 20 hours, the tube being placed in a boiling brine bath at about 105° throughout. The tube-contents were worked up in two ways in each case; a portion was poured into hot very dilute hydrochloric acid (which dissolved it better than plain water), and stirred well up, so as to dissolve the whole; the solution was quickly cooled (to avoid possible decomposition by the saponifying action of the hot water), and rendered slightly alkaline with ammonia; the precipitated flakes became crystalline on standing, and were quickly filtered off and crystallised several times from alcohol. The remainder was treated with a small quantity of alcohol so as to obtain a clear solution; a large bulk of ether was then added, and the whole shaken up with dilute ammonia, whereby an ethereal solution of the free base was obtained, from which crystals separated on spontaneous evaporation. By shaking the ethereal solution with acids the base could be withdrawn as a salt usually very sparingly soluble in water, and not readily crystallising therefrom: even the tartrate was very difficultly soluble, forming a thick curdy mass on agitating the ethereal solution of the base with tartaric acid.

The substance obtained finally in all cases showed identically the same properties, and moreover was apparently absolutely identical with the product of the action of benzoic anhydride on morphine, which was carefully compared with it. The melting point of every sample was close to that given by Polstorff, 186°, but invariably a little higher, indicating greater purity, the numbers all lying between 188° and 190·5° (corr.), no difference whatever being noticeable between the substances made by six and by 20 hours' action. The free alkaloid crystallised anhydrous from alcohol of 80—90 per cent.: the following numbers were obtained with two specimens. (A) from the six hours' treatment, (B) from the 20 hours' treatment.

(A) 0.2930 gram gave 0.8090 CO₂, and 0.1480 H₂O.

(B) 0.3030 gram gave 0.8410 CO₂, and 0.1540 H₂O.

	Calculated for (C ₁₇ H ₁₇ NO)(O.C ₇ H ₅ O ₂).	Found.	
		A.	B.
Carbon	75.46	75.30	75.69
Hydrogen	5.47	5.61	5.64

These two specimens were converted into platinum salts (by solution in warm very dilute hydrochloric acid and addition of platonic chloride); the amorphous or indistinctly crystalline precipitates were dried over sulphuric acid and finally at 100°, and then gave the following numbers:—

(A) 0.3375 gram gave 0.0475 Pt = 14.08 per cent.

(B) 0.3970 gram gave 0.0555 Pt = 13.98 per cent.

Calculated for 2{(C₁₇H₁₇NO)(O.C₇H₅O)₂.HCl}, PtCl₄ = 14.13 per cent.

The tribenzoylated base would require . . 12.37 „

A further proof of these products being *di*- and not *tri*-benzoylated morphine, is afforded by the percentages of benzoic acid formed after heating for some hours with alcoholic potash; the benzoic acid was isolated by evaporation to dryness, solution in water, addition of hydrochloric acid and agitation with ether, spontaneous evaporation to dryness, and titration by standard soda; from the neutral or very faintly alkaline fluid left, the benzoic acid was isolated by evaporation to dryness and treatment with water, whereby a notable amount of resinous matter was left undissolved, derived from the action of the potash on the morphine generated during the saponification: the filtered aqueous fluid was then treated afresh with acid and ether, and the nearly pure benzoic acid obtained weighed. On rendering again alkaline with potash, the acid liquid from which ether had extracted the first crude benzoic acid, and boiling afresh with alcohol for several hours, only very minute quantities of benzoic acid were obtained, showing that the saponification was practically complete after the first treatment.

1.404 gram of specimen (A) thus yielded by titration 0.679 gram of C₇H₅O₂; by direct weighing 0.662 gram.

1.011 gram of specimen (B) gave by titration 0.519 benzoic acid, by weighing 0.513 gram.

Calculated yield of C ₇ H ₅ O ₂ .		Found.	
For tribenzoylated morphine.	For dibenzoylated morphine.	By weighing.	By titration.
61.3	49.5	(A) . . 47.2	48.4
		(B) . . 50.7	51.3
		Mean . . 48.95	49.85

It is hence evident that whether benzoic anhydride or chloride be employed to react upon morphine, the end result is that the two benzoyl groups, and only two, are introduced for each nitrogen present, *i.e.*, that *two-thirds of the oxygen in morphine is hydroxylic in character, whilst the other third has some other function*; and that Herr Polstorff was reasoning on an insufficient basis when he supposed that his experiments proved otherwise.

LII.—*Notes on the Purple of the Ancients* (continuation).

By EDWARD SCHUNCK, Ph.D., F.R.S.

3. *Purple Dyeing in Modern Times.*

ALTHOUGH the art of dyeing with shellfish has long been abandoned in the Old World, it is still carried on to some extent in America, especially on the Pacific coasts of Nicaragua and Costa Rica. The process is described in Don Antonio de Ulloa's "*Physical and Historical Account of Southern and North-Eastern America.*" The author says: "On the coasts belonging to the province of Guayaquil the finest purple is found. The animals from which it is derived are contained in shells, about the size of walnuts, and live on rocks washed by the sea. They contain a juice or humour, which is taken out, and yields the true purple. This humour to all appearance serves the animal instead of blood. Cotton, thread, and other delicate materials are dyed with it. It gives a lively and durable colour, which does not lose its lustre by frequent washing, but is rather improved thereby, and does not fade through long-continued use and exposure. Near the port of Nicoya in the province of Guatemala the same kind of shellfish is found, and is used for dyeing cotton. In both places the dyed yarn is employed in making ribands, lace, and other articles, which are afterwards skilfully sewn and embroidered. All such articles are highly prized on account of their fine and rare colour. Various processes are employed for extracting the juice or humour. Some kill the animal. They take it out of its shell, and, having laid it on the back of the hand, press and squeeze it with a knife from the head to the tail, and then separate the expressed juice, the rest of the animal matter being thrown away. They treat in this way a number of animals until they have a sufficient quantity of juice. They then draw through the thread which they wish to dye, and no more is required. But the dyed threads do not show at once the purple colour they should have.

This is not perceived until the whole is thoroughly dry. At first the colour is milk-white, then it becomes green, and finally purple. Others express the juice without killing the animal. They do not take it entirely out of the shell, but only press it so as to cause a certain quantity of humour to be ejected, with which the threads are dyed. The shells are then laid again on the stones from which they were taken. They recover, and after some time give a fresh quantity of juice, but not so much as the first time." (From a note by Schneider in the Appendix to Dieze's German Translation of Ulloa: Leipsic, 1781.)

Of the process of purple dyeing as practised in recent times by the natives of Central America, Squier gives the following account: "Some of the cotton fabrics manufactured by the Indians are very durable and woven in tasteful figures of various colours. The colour most valued is the Tyrian purple, obtained from the *murex* shellfish, which is found on the Pacific coast of Nicaragua. This colour is produced of any desirable depth and tone, and is permanent, unaffected alike by exposure to the sun and to the action of alkalis. The process of dyeing the thread illustrates the patient assiduity of the Indians. It is taken to the seaside, when a sufficient number of shells are collected, which being dried from the sea water, the work is commenced. Each shell is taken up singly, and a slight pressure upon the valve which closes its mouth forces out a few drops of the colouring fluid, which is then almost destitute of colour. In this each thread is dipped singly, and after absorbing enough of the precious liquid, is carefully drawn out between the thumb and finger, and laid aside to dry. Whole days and nights are spent in this tedious process, until the work is completed. At first the thread is of a dull blue colour, but upon exposure to the atmosphere acquires the desired tint. The fish is not destroyed by the operation, but is returned to the sea, where it lays in a new stock of colouring matter for a future occasion." (Squier's "Nicaragua, its People, Scenery, Monuments, &c.," vol. I, p. 286.)

It would, I imagine, be a matter of some interest to the ethnologist to ascertain whether the art of dyeing purple, as above described, was an original invention of the natives of America, or whether it was introduced into the New World by European settlers. None of the books I have consulted in which the subject is referred to, contain any information on this point, nor even the least surmise.

4. *Examination of a Sample of Purple Yarn from Nicaragua.*

Through the kindness of my friend, Herr von Stralendorff, of Manchester, I have obtained a small quantity of cotton yarn and some

calico, which had been dyed quite recently at Realejo, on the west coast of Nicaragua, together with a specimen of the shell of the animal used for the purpose. Herr von Stralendorff's correspondent, Don Mariano Montealegre, of Chinandega, Nicaragua, through whom the specimens were procured, says that the animal is extracted from its shell by means of a pin or other pointed instrument, the blood furnishing the purple dye.

The shell accompanying the dyed articles, which resembles that of the *Purpura Lapillus* of our coasts, but is much larger, belongs, I am informed, to the *Purpura patula* of conchologists. The yarn and calico were of a dull purple, by no means realising the idea usually entertained of the famous Tyrian dye. They were harsh to the touch and emitted a peculiar smell.

Having taken a portion of the yarn, which after drying weighed 24 grams, I treated it with warm dilute hydrochloric acid. The acid liquid was found to contain in solution much magnesium, a little aluminium and iron, together with calcium sulphate, sodium chloride, and a trace of sodium bromide. These salts were probably derived from the sea water with which one may suppose the body of the mollusc to be permeated, and were doubtless the cause of the harsh, disagreeable feeling of the material. The yarn, after the hydrochloric acid had been washed out, was dried and then treated with boiling ether. The ether which had acquired only a slight colour left on evaporation a residue of a pink hue, consisting for the most part of some fatty acid or acids, probably derived from the tissues of the animal. After passing through these processes, the yarn appeared of a brighter purple than before. It was now treated with boiling aniline, which removed the purple colouring matter, itself acquiring a dark greenish-blue colour. The liquid was filtered boiling hot, and the yarn was again treated with boiling aniline, which sufficed to remove the whole of the colouring matter. The yarn after being well washed with alcohol to remove adhering aniline was dried, when it was found to weigh 19.5 grams. It still retained a brown tinge, which underlying the purple may have been in part the cause of the dull appearance of the latter. The aniline on cooling and standing deposited the colouring matter contained in it in the form of a crystalline powder, which, after being filtered off, washed with alcohol to remove adhering aniline and dried, weighed 0.099 gram.

The colouring matter thus prepared has all the properties of punicin from *Purpura Lapillus* described in a former note.

Seen in the mass it appears of a dark purple colour and crystalline. Under the microscope it is found to consist of flat, right-angled tablets mostly with jagged ends, which by transmitted light show colours varying from reddish-purple to bluish-purple, interspersed with small

rhombic crystals which are much darker and appear blue by transmitted light.

It is insoluble in boiling alcohol and ether, slightly soluble in benzol and glacial acetic acid.

It dissolves easily in boiling aniline, giving a purplish-blue solution, which, on cooling, deposits the whole of the colouring matter contained in it. The solution while hot shows an absorption band between C and D with a well defined edge on the side towards the red, but shading off at the opposite side. The band resembles that of a solution of indigo-blue in aniline, but is somewhat narrower, and does not extend so far towards the red. After standing for some time the solution no longer shows any band, whilst the indigo-blue band only disappears on long standing. The substance also dissolves in boiling phenol, giving a sky-blue solution, which on cooling deposits granular masses of colouring matter, still retaining, however, a blue tinge.

It dissolves in concentrated sulphuric acid, yielding a dull purple solution, which shows an absorption band between D and E. On slightly heating the solution or allowing it to stand for some time, the colour changes to a bright green, and the absorption band disappears. The green solution on the addition of water gives a flocculent precipitate of a lively purple and becomes colourless, from which it may be inferred that the substance yields no sulpho-acids soluble in water, such as are obtained from indigo-blue by treatment with sulphuric acid.

Nitric acid diluted with an equal volume of water which easily decomposes indigo-blue, acts very slowly on this colouring matter even on boiling. It disappears gradually with evolution of nitrous fumes, but even after long-continued boiling small purple particles may be detected floating in the liquid. It also resists the action of a strong solution of chromic acid, with which it may be boiled for a long time without disappearing entirely. This behaviour towards potent oxidisers shows what an extremely stable body this is, and may serve to explain the great permanence which the ancient purple dye was known to possess.

In contact with bromine the substance undergoes on standing a complete change. After evaporation of the excess of bromine a yellow mass is left, which is soluble in boiling alcohol. The solution leaves on evaporation a residue consisting of yellow crystalline needles in star-shaped groups.

It dissolves on treatment with an alkaline solution of stannous oxide, and is again deposited on exposing the solution to the air in the form of a blue pellicle.

On being carefully heated the substance is volatilised, only a trace of residue being left. The sublimate which it yields consists of crys-

tals having, when seen under the microscope, the same form and appearance as those described and figured in a previous note. These crystals show by reflected light a bronze-like lustre, while by transmitted light they appear when not too thick of a deep blue colour. A few thin feathery crystals are usually seen among the more regular ones, which are purple by transmitted light. These variations in colour are, I imagine, due simply to the different thicknesses of substance through which the light passes.

I thought it might be of interest to determine the temperatures at which the substance, which there can be no doubt is identical with the punicin described in a previous note, as well as indigo-blue and indirubin, with which it is nearly allied, begin to sublime. For this purpose minute quantities of the three substances were placed on a glass plate, each being surrounded by a thin metallic ring and covered with a thin glass plate, such as is used for microscopic purposes, resting on the metallic ring, and the whole being heated in a hot air bath. The temperature was noted at which the first indication of a crystalline sublimate could in each case be observed on the glass cover under the microscope; this was for indirubin 140° , for indigo-blue 170° , and for punicin 190° . These temperatures lie so far apart that they may serve to characterise the three substances. From indigo-blue, for which alone it could be mistaken, punicin may most readily be distinguished by the characteristic reaction with sulphuric acid above described.

LIII.—*On the Determination of Carbon in Soils.*

By R. WARINGTON and W. A. PEAKE.

It has been long recognised that the amount of organic matter present in soils cannot be accurately determined from the loss on ignition. The hydrated silicates contained in soil retain water even when dried at a temperature far exceeding 100° , but part with this water at a red heat. The loss on ignition is thus always in excess of the carbonaceous matter really present. It consequently becomes necessary to determine directly the amount of carbon in a soil whenever an exact measurement is required of the organic matter present.

A series of determinations of carbon in arable soils from the experimental fields at Rothamsted was made some years ago by Mr. F. A. Manning. The methods he employed were oxidation with chromic acid, and combustion with chromate of lead. These methods gave on the whole nearly agreeing results, the combustion process

generally yielding a slightly higher proportion of carbon. More recently a considerable number of carbon determinations by the chromic acid method have been made in the Rothamsted Laboratory, chiefly by Mr. P. H. Cathcart. We have ourselves lately examined three methods for the determination of carbon in soil, and propose in the present paper to describe the mode of proceeding adopted, and to give examples of the results.

1. *Oxidation with Chromic Acid.*

This method is recommended by E. Wolff in his admirable "*Anleitung zur chemischen Untersuchung landwirthschaftlich wichtiger Stoffe.*" It consists in treating the soil with sulphuric acid and bichromate of potassium, or by preference with a mixture of sulphuric and chromic acids, the carbonic acid evolved being estimated in the usual way. This method is recommended by Fresenius as an alternative to a combustion of the soil with oxide of copper or chromate of lead. It is apparently the method which has been most generally employed in agricultural investigations.

The mode of proceeding employed in the present case has been quite similar to that directed by Wolff. 10 grams of the finely powdered soil are placed in a flask of about 250 c.c. capacity, provided with a caoutchouc stopper, through which pass two tubes, one for the supply of liquids, the other for the delivery of gas. The soil is treated with 20 c.c. of water and 30 c.c. of oil of vitriol; and the whole, after being thoroughly mixed, is heated for a short time in a water-bath, the object in view being the decomposition of any carbonates existing in the soil. Air is next drawn through the flask to remove any carbonic acid which has been evolved. The stopper is next removed, and coarsely powdered bichromate of potassium introduced. In the case of a pasture soil containing 3 per cent. of carbon, 6 grams of bichromate will be found sufficient, a portion remaining undissolved at the end of the experiment. The stopper is then replaced, its supply tube closed by a clamp, and the delivery tube connected with a series of absorbents contained in U-tubes. The first of these tubes contains solid chloride of calcium; the second, fragments of glass moistened with oil of vitriol; the third and fourth are nearly filled with soda-lime, a little chloride of calcium being placed on the top of the soda-lime at each extremity. The last-named tubes are for the absorption of carbonic acid, and have been previously weighed. The series is closed by a guard tube containing soda-lime, with chloride of calcium at the two ends.

The flask containing the soil and bichromate is now gradually heated in a water-bath, the contents of the flask being from time to time mixed by agitation. A brisk reaction occurs, carbonic acid

being evolved in proportion as the soil is rich in organic matter. The temperature of the water-bath is slowly raised to boiling as the action becomes weaker, and is maintained at that point till all action ceases. As bubbles of gas are slowly evolved for some time, it has been usual in these experiments to prolong the digestion for four or five hours. When the operation is concluded the source of heat is removed, an aspirator is attached to the guard tube at the end of the absorbent vessels, and air freed from carbonic acid is drawn through the flask and through the whole series of U-tubes. The U-tubes filled with soda-lime are finally weighed, the increase in weight showing the amount of carbonic acid produced. The object of the chloride of calcium placed on the surface of the soda-lime is to retain the water which is freely given up when the soda-lime absorbs carbonic acid. The second U-tube filled with soda-lime does not gain in weight till the first is nearly saturated; it thus serves to indicate when the first tube requires refilling. The same tubes may be used several times in succession.

It was found in some preliminary experiments that no increase in the carbonic acid evolved was obtained by substituting chromic acid for bichromate of potassium.

The organic matter of the soil appears to the eye to be completely destroyed by the digestion with sulphuric acid and bichromate of potassium; the residue of soil remaining in the flask when washed with water is perfectly white, or the dark particles, if any, are found to be unaltered by ignition, and therefore to be inorganic in their nature. Under these circumstances considerable confidence has naturally been felt in this method. The complete destruction of the humic matter of the soil does not, however, necessarily imply that the carbon has been entirely converted into carbonic acid. The first doubt on this head we owe to an observation made to one of us by Professor Wanklyn. He pointed out that in other known cases of the action of chromic acid on organic matter the oxidation frequently stopped short of the production of carbonic acid, and that while oxidation with chromic acid apparently led to a complete reaction when the carbon was in the form of graphite, it would probably yield other products than carbonic acid when the carbon existed as a carbohydrate. The doubt thus raised as to the correctness of the results yielded by the chromate method made it desirable to check the work already done by the use of other methods for the determination of carbon.

2. *Oxidation with Permanganate of Potassium.*

In the trials with this method 10 grams of soil were digested in a closed flask with a measured quantity of solution of caustic potash

and crystals of permanganate of potassium. The quantity of potash solution finally adopted was 20 c.c., containing 5 grams of potash. 7 grams of the permanganate were found to be sufficient for a soil containing 3.3 per cent. of carbon. Trials were made with various modes of digestion. The plan which answered best was to heat the flask for half an hour in boiling water, and then for one hour in a salt-bath. The flask during this digestion was connected with a small receiver containing a little potash solution, to preserve an atmosphere free from carbonic acid; distillation to a limited extent was allowed during the digestion in the salt-bath. In some experiments the contents of the flask was distilled to dryness in a chloride of calcium bath, but the results obtained by this plan were frequently low and irregular, the caustic potash forming with clay soils a hard mass, which was afterwards attacked with difficulty by dilute acid.

The first part of the operation being completed a caoutchouc stopper carrying a delivery and supply tube was fitted to the flask, which was then connected with the system of U-tubes already described. Dilute sulphuric acid was then poured down the supply tube, a water-bath surrounding the flask was brought to boiling, and maintained thus for one hour, after which air free from carbonic acid was drawn through the apparatus, the U-tubes containing soda-lime being finally disconnected and weighed.

- In the first stage of this method the carbon of the organic matter is converted into carbonate, and probably also into oxalate of potassium (Wanklyn, *Phil. Mag.* [5], 5, 466); in the second stage the oxalate is decomposed by the sulphuric acid and permanganate, and the carbon existing, both as oxalate and carbonate, is evolved as carbonic acid, and absorbed by the weighed soda-lime tubes. Both F. Schulze and Wanklyn have employed permanganate of potassium for the determination of organic carbon, but they have preferred to calculate the amount of carbon from the quantity of permanganate consumed; as, however, by so doing everything oxidisable by permanganate is reckoned as carbon, it seems better to make a direct determination of the carbonic acid formed.

From the amount of carbonic acid found we have to subtract that existing as carbonates in the soil, and in the solution of potash used. For this purpose an experiment is made with the same quantities of soil and potash previously employed, but without permanganate, and the carbonic acid obtained is deducted from that yielded in the experiment with permanganate. If the potash used contains organic matter two blank experiments will be necessary, one with potash and permanganate, and one with soil alone.

A further difficulty arises from the presence of chlorides in the materials, which occasions an evolution of free chlorine when the

permanganate solution is heated with sulphuric acid. This error occurs also with the chromic acid method, but in that case the quantity of chloride is merely that contained in the soil, which is usually very small; in the permanganate method we have also the chloride present in the caustic potash, and this is often considerable. Corrections for chlorine by blank experiments are unsatisfactory, the amount of chlorine which reaches the soda-lime tubes depending in part on the degree to which the chloride of calcium tube has become saturated with chlorine. It is better therefore to remove the chlorine in every experiment by the plan which Perkin has suggested (*Trans. Chem. Soc.*, 1880, 121), by inserting a tube containing silver foil, maintained at a low red heat, between the flask and the absorbent U-tubes.

The amount of carbonic acid yielded by oxidation with permanganate of potassium was found to be considerably in excess of that obtained by oxidation with chromic acid; to ascertain whether these higher results really represented the whole of the carbon present in the soil trials were next made by actual combustion of the soil in oxygen.

3. Combustion in Oxygen.

It appeared that the most convenient mode of carrying out the combustion of soil would be to place the soil in a platinum boat, and ignite it in a current of oxygen in a combustion-tube partly filled with cupric oxide. This plan has proved very successful. A wide combustion-tube is employed, about 20 inches long, and drawn out at one end; the front of the tube is filled for 8 inches with coarse cupric oxide, the hind part is left empty to receive the platinum boat. The drawn out end of the combustion-tube is connected with a series of absorbent U-tubes, quite similar to those employed for the estimation of carbonic acid in the chromic acid method. Between these absorbent vessels and the combustion-tube we at first inserted a tube filled with 7 inches of the chromate-pumice recommended by Perkin (*Trans. Chem. Soc.*, 1880, 121, 457) for the absorption of nitrous fumes, this tube being kept just sufficiently hot during a combustion to prevent the deposition of water. Latterly we have abandoned the chromate tube, and substituted for the chloride of calcium tube employed to dry the gas a three-bulbed Geissler tube filled with oil of vitriol. The oil of vitriol has proved quite effective in retaining nitrous fumes, combustions of nitrogenous soils made with and without the chromate tube giving closely agreeing results. The wide end of the combustion-tube is connected with a gasholder of oxygen; the oxygen gas is made to pass through a U-tube of soda-lime before entering the combustion-tube, to remove any possible contamination of carbonic acid.

In starting a combustion the part of the combustion-tube containing the cupric oxide is brought to a red heat, and oxygen is passed for some time through the apparatus. 10 grams of soil, previously dried, are placed in a large platinum boat, which is next introduced at the wide end of the combustion-tube. The combustion is conducted in the usual manner, a current of oxygen being maintained throughout the whole operation. It is very useful to terminate the whole series of absorbent vessels with a glass tube dipping into water; the rate at which the gas is seen to bubble serves as a guide to the supply of oxygen from the gasholder, the consumption of oxygen varying of course with different soils, and at different stages of the combustion. At the close of the combustion oxygen, or air freed from carbonic acid, is passed for some time through the apparatus to drive all carbonic acid into the absorbent vessels. One experiment can be followed by another as soon as the hind part of the combustion-tube has cooled sufficiently to admit a second platinum boat. The same combustion-tube can be employed for several days, if packed in the usual manner in asbestos.

The presence of carbonates in the soil occasions some difficulty in working the combustion method, as a part of this carbonic acid will, of course, be given up on ignition, and be reckoned as carbon. The simplest mode of meeting this difficulty is to expel the carbonic acid belonging to the carbonates before the combustion commences. We have had but little experience with soils rich in carbonates, the Rothamsted soils containing at most but a very small proportion of chalk. With such soils we have employed the method already made use of by Mr. Manning in his earlier work on the same subject, namely treatment with a strong solution of sulphurous acid. The 10 grams of soil taken for combustion are placed in a flat-bottomed basin, covered with a thin layer of sulphurous acid, and frequently stirred. After a time the action is assisted by a gentle heat. When the carbonates have been completely decomposed the contents of the basin is evaporated to dryness on a water-bath, the dry mass is then pulverised, and removed to the platinum boat for combustion in oxygen. For the action of the sulphurous acid to be complete it is essential that the carbonates should be in very fine powder, even chalk is but imperfectly attacked when present in coarse particles.

A few experiments were made to test the efficacy of this process. Carbon was first determined in the usual way in three soils naturally free from carbonates; chalk, previously ignited at a low heat to destroy organic matter, was then added in quantity equal to 5 per cent. of the original soil. The soil containing the chalk was next reduced to a very fine powder, a quantity of the mixture corresponding to 10 grams of the original soil was treated with sulphurous acid, and

the carbon again determined. The percentages of carbon found were as follows:—

Kind of soil.	In original soil.			After addition of chalk and treatment with sulphurous acid.		
	Exp. 1.	Exp. 2.	Mean.	Exp. 1.	Exp. 2.	Mean.
Old pasture	3·21	3·25	3·23	3·24	3·33	3·29
New pasture	2·33	2·32	2·33	2·32	—	2·32
Clay subsoil	0·29	0·29	0·29	0·31	0·30	0·31

Having thus described the methods which we have examined, we will next submit some numerical results obtained by their use.

Comparison of Methods.

A considerable number of soils analysed by the chromic acid method have been lately re-analysed by the combustion method; the results compare as follows:—

Percentage of Carbon found by two methods in Soils dried at 100°.

No.	Kind of soil.	Chromic acid method.			Combustion method.			Yielded by chromic acid if carbon by combustion 100.
		Exp. 1.	Exp. 2.	Mean.	Exp. 1.	Exp. 2.	Mean.	
1	Old pasture	2·85	2·79	2·82	3·58	3·55	3·57	79·0
2	2·83	2·79	2·81	3·57	3·53	3·55	79·1
3	2·76	2·76	2·76	3·46	3·46	3·46	79·7
4	2·74	2·76	2·75	3·37	3·38	3·38	81·4
5	2·64	2·54	2·59	3·31	3·36	3·34	77·5
6	2·51	2·43	2·47	3·15	3·15	3·15	78·4
7	2·40	2·44	2·42	3·09	3·13	3·11	77·8
8	New pasture	1·92	1·93	1·93	2·41	2·40	2·41	80·1
9	1·66	1·81	1·74	2·39	2·43	2·41	72·2
10	Arable soil	1·78	1·78	1·78	2·14	2·13	2·14	88·2
11	1·21	1·14	1·18	1·40	1·43	1·42	83·1
12	Subsoil	0·28	0·27	0·28	0·37	0·38	0·38	73·7

Of the above soils the arable soils, Nos. 10 and 11, were the only ones containing carbonates in any quantity exceeding a minute trace. The two soils in question were treated with sulphurous acid before combustion, the others not.

All the determinations by the chromic acid method were made by Mr. P. H. Cathcart, with the exception of Nos. 9 and 12, which were

executed by another experimenter, and are seen to give distinctly lower results. Excluding these two analyses the relation of the carbon found by the two methods is tolerably constant, the average being 79.9 of carbon found by oxidation with chromic acid for 100 yielded by combustion in oxygen. The results obtained by the chromic acid method thus appear to be very considerably below the truth.

Four typical soils have been analysed by the permanganate, as well as by the chromic acid and combustion methods. The results obtained were as follows:—

Percentage of Carbon found by Three Methods in Soils dried at 100°.

No.	Kind of soil.	Combustion method.	Chromic acid method.	Permanganate method.			Yielded by permanganate if carbon by combustion 100.
		Mean.	Mean.	Exp. 1.	Exp. 2.	Mean.	
2	Old pasture	3.55	2.81	3.26	3.30	3.28	92.4
8	New pasture	2.41	1.93	2.29	2.30	2.30	95.4
11	Arable soil	1.42	1.18	1.28	1.33	1.31	92.3
12	Subsoil	0.38	0.28	0.34	0.34	0.34	89.5

Oxidation by permanganate thus gives a much higher result than oxidation with chromic acid; but even the permanganate fails to convert the whole of the carbon into carbonic acid, the product with permanganate being on an average of the four soils 92.4 per cent. of that yielded by combustion in oxygen.

Wanklyn states (*Phil. Mag.* [5], 7, 138) that a temperature of 160—180° is necessary in some cases to effect complete oxidation with permanganate and caustic potash. Such a temperature was found impracticable when dealing with soil, from the action of the potash on the silicates present: hence possibly the low results obtained.

Combustion in oxygen appears from these experiments to be the most satisfactory method for determining carbon in soil, nor is this method on the whole longer or more troublesome than the other methods investigated.

We have further determined the loss on ignition of the four soils mentioned above, with the view of comparing this loss with the amount of organic matter calculated from the carbon actually present. In making this calculation we have taken as the amount of carbon in the soil that found by combustion in oxygen, and have assumed with Schulze, Wolff, and Fresenius that 58 per cent. of carbon will be present in the organic matter of soils. The four soils were heated suc-

cessively at 100°, 120°, and 150°, till they ceased to lose weight; the loss on ignition in each of these stages of dryness is shown in the following table:—

Percentage Loss on Ignition compared with Organic Matter calculated from Carbon.

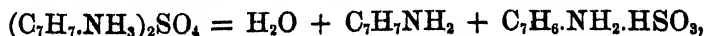
No.	Kind of soil.	Loss on soil dried at 100°.			Organic matter at 58 per cent. carbon.
		Between 100° and ignition.	Between 120° and ignition.	Between 150° and ignition.	
2	Old pasture	9·27	9·06	8·50	6·12
8	New pasture	7·07	6·88	6·55	4·16
11	Arable soil	5·95	5·70	5·61	2·44
12	Clay subsoil	5·82	5·39	4·76	0·65

The loss on ignition is seen to be in all cases very considerably in excess of the organic matter calculated from the carbon, even when the soil has been dried at as high a temperature as 150°. The error of the ignition method is least in soils rich in organic matter, as, for instance, the old pasture soil in the above table. The error reaches its maximum in the case of the clay subsoil, which contains very little carbonaceous matter, but is naturally rich in hydrated silicates, which part with their water only at a very high temperature.

LIV.—*On the Formation of Amidosulphonic Acids by the Action of Concentrated Sulphuric Acid.*

By R. H. C. NEVILLE and A. WINTHER.

IN *Watts' Dict.*, 5, 477, we find that aniline sulphate is converted by gradual heating into phenylsulphamic or sulphanilic acid, but we do not find this process mentioned in any text-books, the use of fuming or Nordhausen sulphuric acid being generally indicated. In the course, however, of some experiments upon orthotoluidine sulphate, we observed that this salt when heated gave off toluidine and water in nearly theoretical proportions, according to the equation:



and on exhausting the residue in the flask with boiling water, and purifying by means of animal charcoal and recrystallisation, we

obtained the acid $C_7H_6(NH_2).HSO_3$ in very nearly theoretical quantity. The plan that we found best was to immerse the flask containing the toluidine sulphate in a bath of fusible metal kept at a temperature of $210-220^\circ$.

We also tried this process upon aniline and paratoluidine: the results obtained from the former were very good, but from the latter very bad, indeed we could scarcely obtain any acid from it; we did, however, get a small quantity. We now tried the effect of increasing the amount of sulphuric acid so as to form an acid sulphate of toluidine, $C_7H_7NH_3.HSO_4$, and heating this salt. We thus obtained from the acid sulphate of orthotoluidine a still better yield than from the normal sulphate, the whole or nearly the whole of it being converted into acid in accordance with the equation:



accompanied by a very small quantity of red colouring matter, which was formed in much larger quantities when the normal sulphate was employed. Aniline gave equally good results; and in the case of paratoluidine, we found that, whereas the normal sulphate yielded scarcely any acid, the acid sulphate gave a good yield, not so good certainly as in the case of orthotoluidine, but still a very fair amount.

The temperatures we found best in the metal-bath were for—

Paratoluidine	220—240°
Orthotoluidine	220—230°

but in using the acid sulphate we frequently heated it on a sand-bath till the mixture became fluid, continuing to heat it, with constant stirring, until it again became quite solid. We also tried naphthylamine. The normal salt of this base behaved like that of paratoluidine, but on heating the acid salt to $180-200^\circ$, we obtained the amidonaphthalenesulphonic acid.

Orthoamidotoluenesulphonic Acid.—The acid obtained by the above process from orthotoluidine gave white crystals, which when dried in air contained one molecular proportion of water. Two experiments gave 8.62 per cent. and 8.65 per cent. respectively, the theoretical amount being 8.78 per cent. They gave off this water when heated to 100° , and the acid then gave on analysis:—

		Calculated for $C_7H_6NH_2.HSO_3$.
C	44.46	44.92
H	4.95	4.81
SO ₃	43.32—42.64	42.78

It forms salts more easily soluble in water than the acid itself. We obtained the potassium salts in glittering tables and prisms with one

molecular proportion of water; the sodium salt in glittering tables with four molecular proportions; the barium salt in tables and prisms with seven; the silver salt in colourless anhydrous prisms; and the lead salt in long flat prisms.

It would be natural to suppose that the acid obtained in this manner would be identical with that which is produced by heating the ethyl-sulphate of orthotoluidine, this latter being described by Limpricht and Pagel (*Jahresb. f. Chem.*, 1874, 701) as identical with that which Gerver mentions as produced by the action of fuming sulphuric acid upon toluidine (*ibid.*, 1873, 672), and probably consisting of orthoamidotoluenemetasulphonic acid. We however find certain differences, and not unimportant ones.

Gerver says that, on the addition of bromine to an aqueous solution of his acid, tribromotoluidine is precipitated (melting after purification by distillation with steam at 112°), the dibromamidosulphonic acid remaining in solution. This is not the case with our acid.

On adding an aqueous solution of bromine slowly to an aqueous solution of the acid to the extent of not more than one molecular proportion of bromine, a slight reddish opalescence is all the change produced in the liquid; and if it be then boiled, filtered, and evaporated, the bromamidosulphonic acid crystallises out, but it is a mono- and not a di-bromamidosulphonic acid. On analysis it gave 29.88 per cent. bromine. Theory for $C_7H_5.NH_2.Br.HSO_3$ requires 30.07 per cent.

On further addition of bromine a copious flocculent precipitate was produced, at first yellowish-white, but generally changing rapidly to green, and then to dark red or brown.

On distilling this precipitate two or three times in a current of steam, we obtained a perfectly white substance, which crystallised from ether in long needles, melting at $45-46^{\circ}$, and in every respect identical with the dibromotoluidine $C_6H_3.NH_2.Br.H.Br.H$, described by us in a former communication to the Society (p. 436 of this volume).

Analysis.

$Br = \frac{60.16}{60.47}$ per cent. Mean = 60.32 per cent.

Theory for $C_6H_3.CH_3.NH_2.Br_2$ requires 60.37 per cent.

We also noticed some minor differences between our acid and that described by Gerver, especially the water-content of some of its salts; but we do not attach much importance to this, as we found that, in the case of at least one, viz., the barium salt of monobromotoluenesulphonic acid, we could make it crystallise with quantities of water ranging from 1 to 7 per cent., by varying the degree of concentration

of the hot solution. This would correspond with a difference of from less than half a molecular proportion to more than two and a half. We can only account for the discrepancy between our results and those of Gerver, by supposing that the orthotoluidine used by him was impure (*loc. cit.*).

Now as to the constitution of this acid: We found the acid obtained by a similar process from aniline to be in every respect similar to that described as sulphanilic acid (Limpricht, *Ber.*, **8**, 1065), and having the constitution $C_6NH_2.H.H.HSO_3.H.H$; and it would therefore be probable that in this acid the sulpho-group would go into the meta-position to CH_3 , and the para-position to NH_2 , so that the acid would have the constitution $C_6.CH_3.NH_2.H.H.HSO_3.H$. That the sulpho-group goes into the meta-position to CH_3 is certain, 1st, from the production of dibromotoluidine of the constitution $C_6.CH_3.NH_2.Br.H.Br.H$ from it by the action of bromine; 2nd, from the melting points of the sulphochloride and amide, obtained from the toluenesulphonic and bromotoluenesulphonic acids produced from this acid. In investigating this second point we prepared the diazo-compound of the amidosulphonic acid by dissolving it in water, allowing it to cool and transmitting a current of nitrous gas through the solution. The diazo-compound was then immediately precipitated, and by stopping the current as soon as the whole mass became thick, then filtering and slightly washing, a nearly theoretical yield was obtained. This compound formed a white slightly explosive powder, exploding either by a heat of about 100° , or by friction, but with little force, and leaving a carbonaceous residue. By heating this compound upon a water-bath with a concentrated solution of hydrobromic acid, it was decomposed, with formation of bromotoluenesulphonic acid. By treating the potassium salt of this acid with phosphoric chloride, we obtained the sulphochloride, melting at $55.6-56.6^\circ$, and this agrees nearly with the bromotoluenesulphochloride described by Hübner and others (*Jahresb.*, 1870, 747; 1871, 675; 1872, 594; 1873, 658) as having the sulpho-group in the meta-position to CH_3 . The chloride heated with ammonia gives an amide melting at $146.3-147.2$.

We also prepared the toluenesulphonic acid in two ways, viz.: (1) by heating the above orthodiazotoluenesulphonic acid under pressure with alcohol; and (2) by reducing the above bromotoluenesulphonic acid by means of sodium-amalgam. By both of these methods we obtained a toluenesulphonic acid which gave, on treating its potassium salt with phosphoric chloride, a liquid sulphochloride yielding with ammonia an amide (m. p. $106.5-107.5^\circ$).

Beckurts (*Jahresb.*, 1877, 943) finds the melting point of toluene-orthosulphonamide to be $153-154^\circ$, and that of tolueneparasulphonamide to be 137° . He also finds a sulphonamide melting at 104° ,

which he considers to be metasulphonamide, but later investigations (*Ber.*, 1879, 1048; 1880, 1292) have shown that in all probability the product which he obtained was a mixture of two sulphonamides, ortho and para, melting, as such mixtures not unfrequently do, below the melting points of either of its constituents when pure. It appears however that the melting point he obtained was nearly right for meta-sulphotoluene, inasmuch as the toluenesulphonic acid which we obtained by either of the above methods, or, as will be seen later, by similar methods from paratoluidine always gave an amide melting at 106.5—107.5°. We think, therefore, that there is no doubt that the acid is orthamidotoluenemetasulphonic acid. The only question remaining is as to whether the sulpho-group is ortho or para to the amido-group. Arguing from sulphanilic acid which Limpricht and Nölting have shown to have the amide and sulpho-groups para to each other (*Ber.*, 8, 1065—1093), we should suppose the same to obtain here, but we endeavoured to determine the question more exactly. We tried :—

1. To convert the orthobromotoluenemctasulphonic acid into dibromotoluene by converting it first into sulphobromide with phosphorus pentabromide, but the reaction did not appear satisfactory.

2. To form from the above-described metabromometasulphotoluidine a diazo-compound, and from this a metabromocresolmetasulphonic acid, and we succeeded well so far, but on heating it with water to take out the sulpho-group the whole appeared to be decomposed, forming different bromocresols and dibromocresols, making this reaction apparently useless.

3. We also tried heating the metabromorthodiazotoluenemetasulphonic acid with dilute nitric acid in the hope that it might form a bromonitrocresol in the same way that the orthodiazotoluenesulphonic acid forms a dinitrocresol, but here again we were doomed to disappointment, as we could not so arrange matters that the sulpho-group alone should be dislodged by the nitro-group. We always obtained dinitrocresol and a mixture of various brominated cresols.

4. The fourth plan we tried gave rather more satisfactory results. In a former communication (p. 435 of this volume) we have shown that the bromine in the ordinary monobromorthotoluidine (m. p. 55—56°) has the bromine in the para-position to NH_2 .

If then, we could remove the sulpho-group from metabromometasulphorthotoluidine, we hoped to be able to ascertain the correspondence or divergence of the body so obtained with or from that above ascertained to have the constitution $\text{C}_6\text{H}_4\text{NH}_2\text{H.H.Br.H}$.

For this purpose we heated the bromamidosulphonic acid to 160° in a sealed tube with hydrochloric acid and water for several hours, and so removed the sulpho-group, but instead of obtaining, as we had

hoped, a monobromotoluidine, we got a certain quantity of a substance (m. p. 43—44°) which proved to be dibromorthotoluidine (analysis gave 60·87 per cent. Br, instead of 60·38 per cent.,) and two monobromotoluidines,—one an oil; (the hydrobromide of this oil gave 30·16 per cent. Br as HBr., monobromotoluidine hydrobromide requires 29·96 per cent.)—and the other a body melting at 54—57°, which appeared to be the ordinary monobromorthotoluidine. Analysis of this latter gave 43·91 per cent. Br. instead of 43·01 per cent. It appeared, then, that whichever monobromotoluidine was first formed, it was decomposed partly into dibromotoluidine and toluidine, and partly into an isomeric monobromotoluidine.

We now tried whether the ordinary monobromorthotoluidine was decomposed by heating with water or hydrochloric acid, and heated it for many hours to 170° and over, but failed to find any change on opening the tube.

Our next step was to endeavour to prepare monobromotoluidine of the constitution $C_6H_5.NH_2.Br.H.H.H$.

For this purpose we took metabromometacetoluide and nitrated it with a mixture of 2 vols. nitric acid, sp. gr. 1520, and 1 vol., sp. gr. 1450. The aceto-group was then removed from the nitrated compound by dissolving it in a freshly-made mixture of 2 vols. sulphuric acid and 1 of water. The metabromorthonitrometatoluidine so obtained melts after purification at 87—88°.

Analysis. Employed 0·0774 AgBr = 0·0624 = 34·30 per cent. Br; theory for $C_7H_5.Br.NO_2.NH_2$ requires 34·58 per cent.

From this we prepared metabromorthonitrotoluene by means of a solution of nitrous gas in alcohol. This distilled with steam as an oil, and gave on reduction with tin and hydrochloric acid a liquid monobromotoluidine.

Analysis. Employed 0·2228 AgBr = 0·2290 = 43·73 per cent. Br; theory for $C_7H_5.Br.NH_2$ requires 43·01 per cent. Br.

We have assumed that, from its method of formation, it must have the constitution $C_6H_5.NH_2.Br.H.H.H$, following the rule laid down in our communication above referred to; but in order further to prove it we added bromine-water to its hydrochloric acid solution, and obtained a compound, melting after distillation with steam at 46—47° (dibromorthotoluidine melts at 45—46° and dibromoparatoluidine at 78°); this shows that it must be a metabromorthotoluidine, and as it is different from $C_6H_5.NH_2.H.H.Br.H$, it must be $C_6H_5.NH_2.Br.H.H.H$. We now heated this liquid monobromotoluidine (which did not solidify in a cold mixture even when a crystal of the other was added to it) with hydrochloric acid in a tube for about 12 hours to 160°, and on distilling the contents with steam we obtained a substance melting at 40—47°. On neutralising the

residue in the flask and continuing the distillation, we obtained a mixture of an oil and of crystals melting at 53—55° (the melting point of the ordinary monobromotoluidine is 55—56°). We may then safely conclude from these experiments that the bromamidosulphonic acid has the constitution $C_6H_4.CH_3.NH_2.Br.H.HSO_3.H$, and that, on heating this acid with hydrochloric acid, the sulpho-group is taken out, but that at the same time the monobromotoluidine of this constitution, not being stable, changes partly into dibromotoluidine and toluidine, and partly into the isomeric monobromotoluidine.

The orthamidotoluenemetasulphonic acid is converted into orthotoluidine either by fusing with alkalis or by heating with water or hydrochloric acid in a sealed tube to from 180° to 200°. If it be heated with orthotoluidine to a temperature of about 235°, it is converted into a fine red colouring matter, dyeing a red shade on silk and soluble but slightly in water, freely in alcohol.

The orthodiazotoluenemetasulphonic acid is easily changed by boiling with water into orthocresolmetasulphonic acid, which by drying in a vacuum over sulphuric acid forms very deliquescent needles, and when heated with water to 130—145° is split up into orthocresol (m. p. 29·8—30·4) and sulphuric acid.

If the diazosulphonic acid or the cresolsulphonic acid be heated with dilute nitric acid, sp. gr. 1·360, about 1 part to 2 or 3 of water, it is converted into dinitroorthocresol, crystallising from alcohol in long yellow prisms which melt at 85·8°. It is easily distilled with water and forms deeper-coloured salts. Its constitution, as will be seen from the above experiment, is $C_6H_3.OH.NO_2.H.NO_2.H$.

Paramidotoluenemetasulphonic acid, obtained in a similar way from paratoluidine by heating the acid sulphate, formed slightly yellow crystals. By treating it in a similar way to the ortho-compound, we obtained from it a toluenemetasulphonic acid which gave an amide melting at 106—107°, whether obtained by heating the diazotoluenesulphonic acid with alcohol, or by the reduction of the bromotoluenesulphonic acid. From this it follows that its constitution is $C_6H_4.HSO_3.NH_2.H.H$. It is much less soluble in cold water than the ortho-compound, and gives salts of much the same character.

The paradiazosulphonic acid is much more soluble in water than the ortho-compound, and it was found necessary to suspend the anido-compound in alcohol instead of dissolving it in water for its formation. By heating it with hydrobromic acid parabromotoluenemetasulphonic acid was obtained, and this gave a chloride melting at 61—62° and an amide melting at 151·5—152·3°.

By heating the diazo-compound with dilute nitric acid, dinitroparacresol, melting at 79—80°, was obtained.

By the action of bromine upon the paramidotoluenesulphonic acid

we obtained a monobromamidotoluenesulphonic acid and a dibromotoluidine, but the bromine did not act so precisely as in the case of the ortho-compound, much dibromotoluidine being always formed, even from the very first. The dibromotoluidine thus obtained melted at 73° , and agreed entirely with that obtained by us from paratoluidine by the action of bromine, and shown (*Chem. Soc. J.*, 1880, 436) to have the constitution $C_6H_4Br.NH_2.Br.H$. This affords an additional proof of the constitution of the sulphonic acid. The above experiments, then, point to the conclusion that, on introducing HSO_3 by this method into an amido-compound, it follows the laws indicated by us for bromine, &c., and goes into the *para*-position with regard to the NH_2 when it can, and in the contrary case into the *ortho*-position.

Naphthylaminesulphonic Acid.

This compound was obtained in a similar manner to the above. In purifying it, we found that the acid itself was so little soluble, even in boiling water, that it was necessary to neutralise it with sodium carbonate, evaporate to dryness, powder, and boil with alcohol to extract all the naphthylamine and colouring matters formed. We then purified the salt by recrystallisation, finally precipitating the acid with hydrochloric acid.

We found that by heating with water to 150° or 160° it was split up into naphthylamine and sulphuric acid. By introducing nitrous gas into the amido-acid made into a pulp with water, we obtained the diazonaphthalenesulphonic acid as a bright-yellow powder in almost theoretical quantity. It is nearly insoluble in cold water. When boiled with water it is slowly decomposed, very little naphtholsulphonic acid however being formed, but a considerable quantity of a crimson colouring matter, which dyes a fine red shade on silk, and can be precipitated as a lake by tin oxide. The formation of this colour can, however, be to a great extent prevented by using strong hydrochloric or dilute sulphuric acid to heat the diazo-compound with, α -naphtholsulphonic acid being then obtained. If stronger sulphuric acid be used, or if the diazo-compound be heated with water to 150° or 160° , α -naphthol is obtained melting at 94° .

If the diazo-compound be heated with dilute nitric acid (about 1 to from 4 to 9) large quantities of dinitronaphthol are formed (m. p. $137-138^{\circ}$).

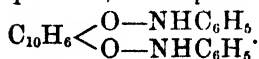
We also prepared sulphonic acids in a similar manner from xylydine and dimethylaniline, but only in small quantities, in order to ascertain whether the same reactions took place, and we did not further investigate the products.

LV.—*On the Action of Ammonia and the Amines upon Naphthoquinone.*

By R. T. PLIMPTON, Ph.D.

THE importance of a study of the ammonia- and amine-compounds of the quinones, as a means of throwing further light upon the question of the constitution of these latter bodies, has been pointed out by G. Schultz (*Ber.*, **10**, 1791), who commenced an investigation of the so-called *quinonamines*, and more recently by Zincke.

It has been supposed that the oxygen-atoms of a quinone determine its reaction with ammonia and the amines, even in cases in which water is not eliminated in the combination; and that the nitrogen-group becomes attached to the carbon-atoms of the quinone only indirectly by means of oxygen. Thus, Wichelhaus (*Ber.*, **4**, 851) has assigned to one of the best-known members of the class in question, the quinone anilide of Hofmann, the structural formula



The subject of the probable difference in constitution of the ammonia derivatives of the quinones, according as these latter possess the structure assigned to them by Graebe, or are double ketones as supposed by Fittig, has been discussed recently at length by Professor Zincke, of Marburg (*Ber.*, **11**, 1999).

The material at his disposal was, however, too scanty to allow of any positive conclusions being drawn in the matter. At the instance of Professor Zincke, I undertook a study of naphthoquinone in the direction indicated, the results of which I now beg to lay before the Society.

The naphthoquinone used was the variety *a*, melting at 125°. The results obtained show that this quinone differs materially in its behaviour to ammonia and the amines from phenanthraquinone and anthraquinone; also from the quinone $\text{C}_{16}\text{H}_{10}\text{O}_2$, of Zincke and Breuer. Moreover, it does not react in quite the same way as common quinone, which in other respects it so closely resembles.

I find, namely, that by the action of primary monamines upon naphthoquinone in alcoholic solution, compounds are formed which consist of 1 mol. of quinone, plus 1 mol. of amine, minus 2 atoms of hydrogen. The methylamine, ethylamine, aniline, and paratoluidine derivatives may, therefore, all be represented by the general formula $\text{C}_{10}\text{H}_6\text{O}_2\text{NR}'$.

Secondary amines react necessarily in a somewhat different manner. Compounds were obtained with dimethylamine, and in presence of

hydrochloric acid, with diphenylamine. The dimethylamine compound on analysis gave numbers agreeing closely with those required by the formula $C_{10}H_5N(CH_3)_2O_2$.

Diphenylamine does not appear to react upon naphthoquinone in alcoholic solution, or even when the substances are melted together. In presence of hydrochloric acid, a dark purplish-blue compound is formed at once, either in presence of alcohol, or when the two substances are heated with dilute hydrochloric acid alone. The analysis of this substance, which was troublesome to purify, gave numbers which agree either with the formula $C_{10}H_5N(C_6H_5)_2O_2$ or with $C_{10}H_5O_2N(C_6H_5)_2$, which would have to be doubled. I have not been able to decide what part the hydrochloric acid plays in the formation of this compound. Experiments described later seemed to negative the hypothesis that a chloroquinone is first formed, which then reacts with the amine.

Tertiary amines do not appear to react on naphthoquinone even in presence of hydrochloric acid.

The whole of the compounds mentioned may be obtained from naphthoquinol instead of from the quinone; the reaction then proceeds more slowly, and oxidation is observed on the surface of the liquid.

It is worthy of remark that it is not necessary to use the amines in the free state; indeed, it is advantageous in the preparation of methyl-, ethyl-, and dimethyl-amine derivatives, to neutralise the amine solution with acetic acid before adding it to the naphthoquinone. In this way a purer product is obtained.

These compounds crystallise well in needles, which possess a brilliant lustre, and may be sublimed unaltered.

The naphthoquinone used for the following experiments was obtained by the oxidation of naphthalene dissolved in glacial acetic acid by chromic acid (Groves, this Journal [2], 11, 209). It was found advantageous to proceed as follows:—Naphthalene in portions of 5 grams was dissolved in glacial acetic acid (30 grams for each portion of naphthalene), 15 grams of chromic acid was then added little by little to each flask, and a brisk action kept up by means of gentle heating, until the whole of the chromic acid had been added. The mixture was then boiled for a few minutes and precipitated with water, the precipitate filtered off, distilled with steam, and crystallised from light petroleum, according to the directions of Groves. The yield is about 15—20 per cent. of the naphthalene employed.

I attempted to prepare naphthoquinone in a manner analogous to that given by Nietzki (*Ber.*, 11, 1102) for the preparation of common quinone, and oxidised naphthylamine in the cold, and at the temperature of a water-bath, with potassium bichromate and sulphuric acid,

but without success. In the cold a small quantity was formed, but at 100° the product was a purple-red amorphous body, which contained no trace of the substance sought. Some naphthoquinone was also obtained by oxidation of amidonaphthol with a dilute solution of chromic acid (Liebermann, *Liebig's Annalen*, **183**, 248); the separation of the isomeric α - and β -nitronaphthols by boiling water, a stage in the preparation of amidonaphthol from acetamidonaphthalide is, however, very tedious.

Naphthoquinol.

This body, which Groves obtained by reducing the quinone with strong hydriodic acid, may be readily obtained by throwing powdered naphthoquinone in small portions into a boiling mixture of tin and hydrochloric acid. The substance becomes dark, and after some minutes dissolves, and on leaving the filtrate to cool, the quinol crystallises out in white needles, melting at 173°. Sulphurous acid also reduces the quinone at 140–150°. On boiling the product with water, some naphthoquinol is dissolved out, but a large quantity of an amorphous insoluble body remains.

Compound formed from Naphthoquinone and Aniline.

I have been able to study this compound more fully than the others, on account of the ease with which it can be prepared. I therefore describe it first.

Preparation.—If an excess of aniline be added to an alcoholic solution of naphthoquinone, the liquid immediately becomes red, and after some minutes' heating on the water-bath, the reaction is ended. Water is then added, together with some acetic acid, the liquid well shaken and filtered. The precipitate is dissolved in alcohol, boiled with some animal charcoal to free it from small quantities of dark substances which are generally formed (especially if the mixture has been heated too long), and crystallised once or twice, from dilute alcohol. Thus prepared, it forms beautiful red needles of great brilliancy, which melt at 190–191°, and at a higher temperature sublime undecomposed.

The aqueous filtrate containing acetic acid deposits, on standing in the air, considerable quantities of the red compound.

It is best to use a considerable excess of aniline, about double the weight of the naphthoquinone employed. With smaller quantities of aniline, the precipitate is apt to be light in colour, and to contain undecomposed quinone.

The aniline compound dissolves easily in hot alcohol, benzene, and

ether, less so in cold alcohol. In light petroleum it is almost insoluble.

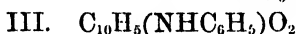
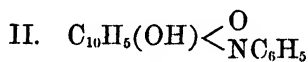
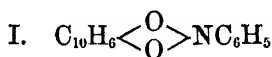
Concentrated sulphuric acid dissolves it, with production of a splendid crimson colour; water precipitates the compound apparently unaltered.

Alcoholic potash dissolves it with a purple colour: the solution can be evaporated to dryness without decomposition, and the remaining brown mass on becoming moist rapidly absorbs oxygen, and regains its purple colour.

The aniline compound, and indeed all the amine derivatives of naphthoquinone, burn with great difficulty, and combustion with oxide of copper generally gave results much too low. Of the following analyses, Nos. I and II were made with this material, the second, however, in a stream of oxygen. III and IV were made with chromate of lead.

	I.	II.	III.	IV.	Calculated for $C_{16}H_{11}NO_2$.
C....	68.01	76.75	76.35	77.44	77.10
H....	4.68	4.38	4.71	5.09	4.41
N....	—	—	—	5.75	5.62

The nitrogen was estimated by Dumas' method. These numbers agree with the formula, $C_{16}H_{11}NO_2$, which may be resolved into—



A body of the composition II, and perhaps III also, should give an acetyl-derivative with acetic anhydride; the substance was therefore heated for several hours in a sealed tube with acetic anhydride to 150—160°, and in a second experiment to 170°, but it remained unaltered. Benzoic anhydride did not attack the substance when heated with it in a test-tube.

A compound of formula II might also be expected to split into oxynaphthoquinone and aniline when heated with hydrochloric acid. Some of the red crystals heated to 160—170° with hydrochloric acid were completely decomposed, with formation of a black substance. The filtrate from this substance was evaporated and found to contain aniline, but the black substance which was similar to that obtained by heating naphthoquinone with strong hydrochloric acid, did not contain any oxynaphthoquinone.

In a second experiment the substance was boiled with hydrochloric acid and alcohol, till the colour had quite disappeared, then evaporated

down, and after addition of a little water, shaken with ether. The residue left by the ether on evaporation was yellowish, and no oxynaphthoquinone was found in it. On standing, the red compound was gradually reproduced. The aqueous solution on evaporation was found to contain aniline.

There remain the formulæ, $C_{10}H_6O > NC_6H_5$ and $C_{10}H_6(NHC_6H_5)O_2$.

It was thought probable that if the former were correct, the compound could be reduced to naphthoquinol and aniline. Experiments were made with zinc and hydrochloric acid and with sulphurous acid in aqueous and alcoholic solution.

The red crystals were heated to 125–130° with aqueous sulphurous acid for some hours, and the resulting yellowish solution filtered from an undecomposed residue. On evaporating the filtrate and allowing it to stand, red needles melting at 190–192° soon appeared on the surface.

To compare the action of naphthoquinol and aniline, solutions of each in water were mixed and allowed to stand in the air. Red needles soon formed on the surface, which possessed all the properties of the anilide. Some of the anilide was then heated to 130° with sulphurous acid, the liquid quickly filtered and made acid with hydrochloric acid. Ether dissolved from this solution a substance which remained after evaporation of the ether in blackish needles, which melted at 165°. The aqueous solution contained aniline. The needles did not appear to be the quinol, as no naphthoquinone could be obtained from this by oxidation.

At 150° to 155°, the reaction with sulphurous acid is more complicated, a quantity of black substance is found mixed with melted globules of sulphur and white needles, which oxidise at once in the air.

Zinc and hydrochloric acid boiled with naphthoquinone anilide decolorise it, and on addition of water a reddish-white precipitate falls, which rapidly oxidises in the air to the original compound. In a second experiment the liquid was shaken out with ether as soon as decolorisation had taken place. On evaporating the ether, a reddish mass was left which soon gave again the red compound (m. p. 188°). The liquid contained aniline.

Whether the reddish substance is a single reduction-product or a mixture could not be decided, on account of the small quantity at disposal.

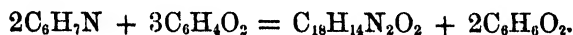
A white reduction-product is also obtained by reducing the anilide in alcoholic solution with ammonium sulphide. The reagent is added in large quantities, and after some time white crystals are formed, not, however, needles (naphthoquinol). The substance may be washed

with dilute ammonium sulphide, but oxidises too rapidly for analysis. The red compound appears to be reproduced.

The ease with which the aniline compound is decomposed, with separation of aniline, by sulphurous acid and hydrochloric acid, appeared to favour the adoption of the formula $C_{10}H_6<\overset{O}{O}>NC_6H_5$. The analysis of the dimethylamine compound subsequently obtained agrees, however, with the formula $C_{10}H_5N(CH_3)_2O_2$, according to which the nitrogen must be supposed directly combined with carbon. The aniline body, probably similarly constituted, must then be represented by the formula $C_{10}H_5(NC_6H_5H)O_2$. The facts obtained do not allow of a decisive conclusion on this point.

In the reaction between naphthoquinone and aniline, two atoms of hydrogen are eliminated for each molecule of the quinone; the same takes place with benzoquinone, if the formula given by Wichelhaus is correct.

Hofmann's formula contains two atoms of hydrogen less (*Watts's Dict.*, 4, 426), and he represents the reaction by the following equation:—



The four atoms of hydrogen eliminated, therefore, go to form quinol, which is found in the mother-liquid after the reaction.

As already mentioned, during the preparation of naphthoquinone-anilide, the mother-liquid deposits on standing considerable quantities of the substance; this may be explained if naphthoquinol be a product of the reaction, for it has been shown that the latter body reacts with aniline in aqueous solution. Attempts to separate naphthoquinol were, however, unsuccessful. Once only long white needles were observed, very soluble in alcohol. The dark substances formed in small quantity are probably reduction-products of naphthoquinone: common naphthoquinhydrone is not formed. Another explanation must be sought for to account for the disappearance of two atoms of hydrogen; possibly a simple addition-product of 1 mol. of quinone and 1 mol. of aniline is formed which then quickly oxidises in the air. I noticed, indeed, that the compound when first precipitated by water is lighter in colour.

The aniline compound remains unacted upon by aniline when heated with it in alcoholic solution to 200°.

Paratoluidine Compound.

The paratoluidine-compound, which is very similar to the preceding,

was obtained by heating 1' molecular proportion of naphthoquinone with rather more than 1 molecular proportion of paratoluidine in alcoholic solution for some minutes, and precipitating with water and acetic acid. The precipitate was purified by dissolving in alcohol, boiling with a small quantity of animal charcoal, and crystallising once or twice from dilute alcohol. It crystallises in red needles which melt at 200°.

A combustion with oxide of copper in a stream of oxygen gave the following numbers:—

	Found.	Calculated for $C_{10}H_6O_2NC_6H_4(CH_3)$.
C. . . .	77·65	77·56
H . . .	5·14	4·94

The colourless filtrate obtained in the preparation of this body gives, on standing, further quantities of red needles, just as in the case of the aniline derivative.

Concentrated sulphuric acid dissolves the toluidine-derivative with a fine purple colour.

With orthotoluidine, naphthoquinone also gives a compound very soluble in alcohol. I have not obtained it in a pure state.

Compound with Methylamine.

The methylamine and ethylamine-derivatives are not quite so easy to prepare as the preceding, for it was found difficult to prevent the formation of dark-coloured bye-products, the removal of which caused loss of time and material.

If a solution of methylamine (33 per cent.) is added drop by drop to a small quantity of naphthoquinone dissolved in alcohol, and the test-tube warmed for a minute or two very gently, the liquid becomes red, and on addition of water and acetic acid the compound separates out in small bright red needles. If, however, the experiment is made with larger quantities, the result is a brown or nearly black liquid, which gives on precipitation a brown and very impure precipitate. This is also the case when the warming is avoided.

In one experiment 5 grams of naphthoquinone were dissolved in 50 grams of alcohol, and, drop by drop, 10 grams of methylamine solution (33 per cent.) added; the mixture was heated gently for five minutes, and then precipitated with water and acetic acid. The precipitate was brown, and the filtrate appeared to contain quinol, for, when heated with more methylamine solution a further precipitate was obtained. As it was suspected that the precipitate also contained reduction-products of the quinone, it was dissolved in alcohol, filtered from an insoluble brown substance, and again heated with some methylamine solution and a few drops of acetic acid. By precipita-

tion with water a substance was obtained of a redder colour, and this precipitate was therefore again subjected to a similar treatment.

The substance partially purified by this means was boiled in alcoholic solution for a long time with charcoal; the filtrate then deposited small red needles.

The aqueous liquids, acid with acetic acid, obtained during the treatment of the precipitate with methylamine and acetic acid, gave on evaporation small quantities of a black substance soluble in alcohol, which, when oxidised with chromic acid and acetic acid, was converted into an orange-coloured body precipitated by water. This substance, which was not quinone, possibly belongs to the class of dinaphthoquinhydrones obtained by Stenhouse and Groves (*Liebig's Annalen*, 194, 202) by the action of acids on β -naphthoquinone. Further experiments showed that it is better to act upon naphthoquinone with a methylamine salt than with the free amine. The quinone is dissolved in alcohol, and then an excess of methylamine solution first neutralised with acetic acid, is added, and the mixture evaporated nearly to dryness. Water is added, and the precipitate filtered off, dissolved in alcohol, and boiled with animal charcoal until a small portion filtered off shows a red colour.

The needles which separate on cooling have a bright red colour and brilliant lustre. They melt at 232° (uncorr.), and are easily soluble in alcohol.

Analysis gave the following numbers:—

	I.	II.	Calculated for $C_{10}H_6O_2NCH_3$.
C. . . .	69.98	70.72	70.59
H . . .	5.03	Lost	4.81
N. . . .	7.25	—	7.48

The combustions were made with chromate of lead, and the nitrogen was estimated by Dumas' method.

The methylamine derivative is also reduced by sulphurous acid in aqueous solution at 150° , with formation of white needles, sulphur, and dark substances. The white needles could not be obtained pure, as they oxidise rapidly in the air.

Compound with Ethylamine.

The ethylamine derivative is obtained in the same way as the preceding by using acetate of methylamine and naphthoquinone in alcoholic solution. As might be expected, if instead of working with a nearly neutral solution, much hydrochloric or acetic acid is present, neither the methyl- nor ethylamine derivative is formed, except in very small quantity.

The quinol may be used instead of naphthoquinone itself, and reacts easily with either methyl- or ethyl-amine and their acetates. A dark brown colour forms at first on the upper layer of the mixture, and gradually extends downwards.

The ethylamine compound may be purified by boiling in alcoholic solution with animal charcoal, and crystallises after evaporation of a portion of the alcohol in needles, which are not so red as the methyl-amine compound. Addition of water is not advisable. The needles melt at 139—140°, and sublime unaltered in long needles which have a very brilliant lustre. They are easily soluble in hot alcohol and benzene, but very slightly in light petroleum.

Combustions were made at first with oxide of copper, but the results obtained were much too low. No. III was made with chromate of lead.

	I.	II.	III.	Calculated for $C_{10}H_6O_2NC_2H_5$.
C....	67.12	64.1	71.96	71.64
H ..	5.55	5.57	6.44	5.47
N....	—	—	7.3	6.96

Action of Ammonia on Naphthoquinone.

If ammonia solution be added drop by drop to an alcoholic solution of naphthoquinone, the liquid at once becomes dark brown, and by precipitation by water a brown amorphous body is obtained. With the quinol ammonia reacts more slowly, and on addition of water a red-brown substance separates, which contains no nitrogen. Acetic acid produces a further precipitate, which also contains no nitrogen.

Ammonia apparently acts in the same way as the potassium and sodium hydrate or carbonates, which dissolve naphthoquinone to a brownish-red solution, from which acids precipitate a red substance, the nature of which has not been ascertained. It is, however, doubtless, the so-called "carminaphe" discovered by Laurent, and lately described by A. Guyard (*Bull. Soc. Chim.* [2], **31**, 64), who obtained it by oxidising naphthalene dissolved in acetic acid with chromic acid, and neutralising with sodium carbonate.

I have prepared carminaphe according to the directions of Guyard, in order to ascertain whether, as seemed probable, this substance is the result of the action of the sodium carbonate upon the naphthoquinone formed by the oxidation. In the first experiment made, as soon as the oxidation was finished and the liquid had cooled, it was neutralised with sodium carbonate. Carminaphe was found neither in the precipitate nor in the filtrate, but on distilling the precipitate with steam, much naphthoquinone came over. In a second experiment the neutralisation was effected, on the contrary, in the hot liquid, and

the carminaphe obtained in abundance from the precipitate, and also from the filtrate on adding hydrochloric acid. It is soluble in benzene, and is precipitated on addition of light petroleum as a dark red powder.

Compound with Dimethylamine.

Dimethylamine solution added to alcoholic solution of naphthoquinone, produces a brownish-red coloration, and on addition of water a very small quantity of resinous substance is precipitated. The filtrate, on standing in an open dish, deposits needles of a bright red colour, which melt at 115° , and can be purified by recrystallisation from hot water.

A good method of preparation is to dissolve naphthoquinone in alcohol, add excess of dimethylamine solution (33 per cent.) neutralised with acetic acid, and allow the mixture to stand for a day or so in a large dish. The residue is extracted several times with boiling water, and the crystals obtained purified by one or two recrystallisations. The dimethylamine-derivative forms bright red needles, which melt at 118° .

Analysis gave the following numbers:—

	I.	II.	Calculated for $C_{10}H_6(N(CH_3)_2)O_2$.
C....	71.52	71.99	71.64
H ..	5.66	5.67	5.47
N....	—	7.6	6.96

The dimethylamine compound is easily reduced by tin and hydrochloric acid. If the colourless liquid be shaken out with ether, on evaporation of the latter a reddish-white substance is left, which is converted by ferric chloride into the original compound.

Action of Diphenylamine on Naphthoquinone in presence of Hydrochloric Acid.

Attempts to prepare a compound of diphenylamine and naphthoquinone in alcoholic solution, and by melting the substances together, gave no result. It was observed, however, that on adding hydrochloric acid, and heating to remove the diphenylamine from such a mixture, that a dark violet substance was formed, which on addition of water separated as a black oil, and solidified very slowly.

This substance was heated gently with solution of carbonate of sodium, and then extracted with boiling benzene. On filtering, a small quantity of a blue amorphous substance was separated. The solution was precipitated with light petroleum, and the precipitate, after numerous crystallisations from alcohol, finally obtained in beautiful violet-black needles, melting at 164° . The substance contained no chlorine.

A number of experiments showed that the precipitation with light petroleum was necessary. When the crude product is purified by precipitation from hot alcohol by strong hydrochloric acid, it is obtained solid, but even after the treatment had been repeated several times the substance often separates from alcohol in a pasty condition, and refuses to crystallise after repeated treatment with alcohol.

Finally the following method of preparation proved advantageous. Naphthoquinone and diphenylamine in the proportion of somewhat more than 1 molecular proportion of amine to 1 molecular proportion of quinone are dissolved in alcohol at a gentle heat, and strong hydrochloric acid (about 10 c.c. for 5 grams quinone) added. The mixture is heated on a water-bath for about 20 minutes, precipitated with water, and collected by decantation. On standing, the aqueous liquid deposits further quantities of the substance mixed with diphenylamine.

The semi-solid precipitate is dissolved in alcohol, and filtered from a small quantity of a blue substance, and the hot solution precipitated with hydrochloric acid with vigorous shaking. The now solid substance is warmed with sodium carbonate, and repeatedly precipitated by light petroleum from its solution in benzene, by which the remainder of the diphenylamine is separated. As soon as the substance becomes very crystalline it is recrystallised once or twice from alcohol. It also crystallises well from alcohol containing a little acetic acid, on addition of hot water.

It is not necessary to use alcohol for the preparation of the diphenylamine-compound, as the same black oil is formed by heating naphthoquinone and diphenylamine with hydrochloric acid.

The needles melting at 164° gave on analysis the following numbers:—

	I.	II.	III. CuO.	IV.
C.	78.83	81.64	80.269	80.87
H	5.63	5.18	5.053	5.11
N	—	—	—	4.55

Combustion III was made with oxide of copper, the others with chromate of lead.

The formula $C_{10}H_5N(C_6H_5)_2O_2$, for which the hydrogen results are somewhat too high, requires—

C	81.23
H	4.61
N	4.30

The formula $C_{22}H_{17}NO_2$, containing 2 atoms of hydrogen more, corresponds, however, with 5.19 per cent. H, and is therefore improbable.

The formula $C_{22}H_{16}NO_2$ agrees perhaps best (4.91 H), but would have to be doubled.

Formulæ containing two or more nitrogen groups are inadmissible.

The analytical numbers do not allow of deciding with certainty upon the formula of this compound, which may possess a very complex constitution. It appeared probable that the hydrochloric acid necessary in the preparation of the substance must act by forming a chloroquinone, which then reacted further with the diphenylamine giving such a body as $C_{10}H_6N(C_6H_5)O_2$.

The results of some experiments in this direction did not, however, agree with this hypothesis, when, for example, naphthoquinone is heated in alcoholic solution for some minutes with hydrochloric acid and diphenylamine added to the mixture, no trace of the purple body is produced.

Further in presence of a good quantity of sulphuric acid the reaction also takes place. Hydrobromic acid acts like hydrochloric acid. With chloride of zinc the purple compound is also formed, but together with much insoluble matter.

It was also thought possible that the dye-stuff was merely an oxidation-product of diphenylamine; it should then be produced also by the action of common quinone.

Experiments were therefore made with benzoquinone. This substance was dissolved in alcohol together with a little more than the quantity of diphenylamine requisite to form a mono-derivative, hydrochloric acid added, and the liquid heated for some minutes. The flask was then closed, and left to stand for twelve hours. At the end of this time the contents become originally blue had assumed a brownish tint. By careful addition of ferric chloride the blue compound was reproduced, and on addition of water precipitated as a blue-black oil. The filtrate, on shaking out with ether, yielded a small quantity of quinol. The precipitate when treated with strong hydrochloric acid lost its colour, but this was restored on treating the mass with sodium carbonate. Benzene extracted a substance which was precipitated by light petroleum. Repeated treatment with benzene and light petroleum failed to purify it completely, and it remained resinous. This substance, however, has a totally different colour from that of the naphthoquinone-compound described.

Acetyl-derivative of the Diphenylamine-derivative of Naphthoquinone.

By heating the diphenylamine-compound with acetic anhydride to 120° a brown liquid is obtained, which on decomposing the excess of anhydride with sodium carbonate, yields a yellow crystalline body. This was purified by boiling with animal charcoal and alcohol, and on

evaporating the latter, small yellow crystals melting at 172—173° were obtained. A combustion was made of these crystals, and gave—

		Calculated for $C_{24}H_{19}NO_3$.
C.....	77.30	78.05
H	5.50	5.15

A diacetyl-derivative, $C_{20}H_{20}O_4N$, requires 76.09 per cent. C and 4.9 per cent. H.

If the acetic anhydride had merely eliminated water, an anhydride must have been produced, containing more than 80 per cent. of carbon. This capacity of forming an acetyl-derivative is not, however, easy to reconcile with the formula $C_{10}H_5(N(C_6H_5)_2)O_2$.

Sulphurous acid in alcoholic solution reduces the diphenylamine-compound at 150°. Water precipitates a brown mass, which in alcoholic solution gives the original compound when allowed to stand over hydrochloric acid.

Sulphide of ammonium at once destroys the colour of an alcoholic solution even in the cold. Water precipitates a white substance, which in the air rapidly changes into the original compound.

Tertiary Amines.

These do not appear to react with naphthoquinone alone, or in presence of hydrochloric acid.

I cannot conclude this paper without expressing my thanks to Professor Zincke for his kind assistance and counsel during the progress of this research, which was made in the University Laboratory of Marburg.

LVI.—*Experiments on Germinating Barley.*

By T. CUTHBERT DAY.

THESE experiments were undertaken with the object of throwing some light on the source of the carbonic anhydride produced during the germination of barley, the observations being limited to the earlier stages of germination as carried out in the process of malting. It was proposed, at the same time, to ascertain whether atmospheric nitrogen takes any active part in the germination, and to determine, as accurately as possible, the amount of oxygen absorbed by the grain as compared with the quantity of the same element excreted in the

form of carbonic anhydride. As a result of the inquiry one fact has been elicited, which is of some importance; for as will be seen, it indicates the probable nature of the body, which by its decomposition during germination furnishes the carbonic anhydride:

1. As is well known a considerable quantity of carbonic anhydride is produced during the germination of barley. I made a few preliminary experiments to ascertain the amount of this gas produced, with the main object of finding out the apparatus most suited for the natural germination of the grain during a period of about ten days. It may be as well to notice in passing a few of the results obtained in these preliminary experiments.

The quantity of carbonic anhydride produced varies much under different conditions of temperature and moisture. A moderate elevation of temperature considerably increases the amount of carbonic anhydride formed. The same effect is produced by an increase in the amount of moisture present in the grain. Thus in two experiments on the same barley, germinated at the same temperature, but with different quantities of moisture, the following results were obtained.—In No. 1, 20.17 grams of barley, sprinkled with water during growth, produced 668.8 c.c. of CO_2 ; in No. 2, 20.01 grams of barley (germinated without any sprinkling) produced 596.9 c.c. of CO_2 . Again, two experiments on the same barley with equal quantities of moisture, but grown at different temperatures, furnished the following figures:—In No. 1, 19.88 grams of barley were grown at a temperature of 61.5°F ., and produced 775.6 c.c. of CO_2 ; in No. 2, 20.17 grams of barley were grown at a temperature of 57.4°F ., and gave 668.8 c.c. of CO_2 .

The total quantity of carbonic anhydride produced, varied in all the experiments (made on about 20 grams of barley in each case) from 1.1679 gram = 592.5 c.c. to 1.7107 gram = 867.8 c.c. From this it can be readily calculated that the weight of carbon oxidised to CO_2 varies from 1.55 per cent. to 2.18 per cent. of the weight of barley employed.

The effect of temperature on the amount of carbonic anhydride produced is not the same in all stages of germination; the point at which an increase of heat fails to produce an increase in the quantity of carbonic anhydride is lower at an early stage of germination than at a later stage. I intend shortly to investigate this point more thoroughly.

2. *Does Atmospheric Nitrogen play any active part in the Germination of Barley?*

Some authors have asserted that the nitrogen of the air plays some part in the chemical changes effected in growing barley during ger-

mination. I quote the following passage from G. J. Mulder's *De la Bière*, p. 107:—"Dans la germination une petite quantité du gaz azote de l'air ambiant est absorbée, et De Saussure n'attribue pas cette absorption à une simple cause physique." But this opinion is not generally admitted, and I therefore thought it well to make several careful experiments to determine the point. According to my experiments there does not appear to be any absorption of nitrogen, but if there is, the amount absorbed is so minute as to lie within the limits of experimental error. The experiments were conducted in the following way:—A weighed amount of steeped barley was placed in the flask C (Fig. 1). This flask was divided into mm. on the neck and carefully calibrated. The flask was inverted, with its mouth below the surface of some mercury (B), at the bottom of a large beaker (A) filled with water. T is a thermometer. A small plug of platinum wire (P) of known weight was placed in the neck of the flask to prevent the corns of barley from falling down to the surface of the mercury. The specific gravity of the barley and of the platinum was determined, so that their volume might be deducted from that of the air in the flask. As soon as the apparatus was arranged, the height of the mercury column was read off on the neck of the flask, the barometer and thermometer being observed at the same time; allowance was, of course, made for the column of water above the surface of the mercury in the beaker.

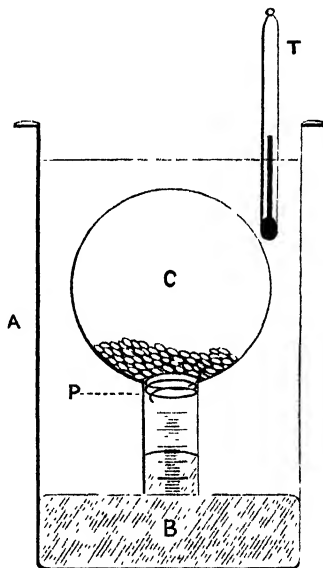


Fig. 1.

At the end of the experiment the same observations were again made, and a portion of the air in the flask was withdrawn for analysis. The following are the results of three experiments performed with this apparatus:—

No. 1. 4.993 grams of Barley.

Vol. of air at commencement of experiment ...	}	98.72 c.c. containing 79.04 per cent. N = 78.03 c.c. N.			
Vol. of air at end of experiment		97.69 " " 79.55 " = 77.72 "			
Decrease....		1.03		Decrease....	0.31
9.128 c.c. of CO ₂ were produced.					

No. 2. 5.352 grams of Barley.

Vol. of air at commencement of experiment ...	{	82.50 c.c. containing 79.04 per cent. N	=	65.21 c.c. N.
Vol. of air at end of experiment	{	81.50 " 80.33 "	=	65.47 "
Decrease....		1.00	Increase....	0.26

4.018 c.c. of CO₂ were produced.

No. 3. 5.345 grams of Barley.

Vol. of air at commencement of experiment ...	{	80.50 c.c. containing 79.04 per cent. N	=	63.69 c.c. N.
Vol. of air at end of experiment	{	79.61 " 80.09 "	=	63.76 "
Decrease....		0.89	Increase....	0.07

4.118 c.c. of CO₂ were produced.

From these results it will be seen that the total quantity of nitrogen in the confined volume of air is sometimes increased, and sometimes diminished to a very small extent. The air used in the experiments was not previously analysed, but was assumed to contain the average amount of nitrogen, *i.e.*, 79.04 per cent. by volume. The result of the experiments certainly seems to prove that nitrogen takes no active part in the germination of barley.

It will be seen that the determination of this point was a necessary prelude to the experiments about to be described.

3. *The Absorption of Oxygen during Germination.*

It has been conjectured, and in certain cases proved, that more oxygen is absorbed by germinating seeds than is required for the production of the carbonic anhydride. In Mulder's *De la Bière* (p. 106) the following passage occurs:—"De Saussure pense que, bien que le fait ne puisse pas toujours être sensible dans les expériences faites dans l'air atmosphérique, la semence s'assimile toujours dans la germination une certaine quantité d'oxygène que l'on ne peut pas retrouver dans l'acide carbonique dégagé." Hellriegel has pointed out (*Journal für praktische Chemie*, 64, 94 [1855]) that oleaginous seeds absorb a very considerable quantity of oxygen, which, at the very commencement of germination, effects an increase in their weight.

It appeared to me that if barley could be grown in such a way as not to lose moisture by desiccation, or if a correction could be applied for loss of moisture by the grain, it would become easy to ascertain whether there is an absorption of oxygen in excess of what is necessary for the disengagement of the carbonic anhydride. The apparatus shown in Fig. 2 was found to answer admirably for this purpose; it is

merely a modified form, with certain additions, of that used in the estimation of the amount of carbonic anhydride produced.

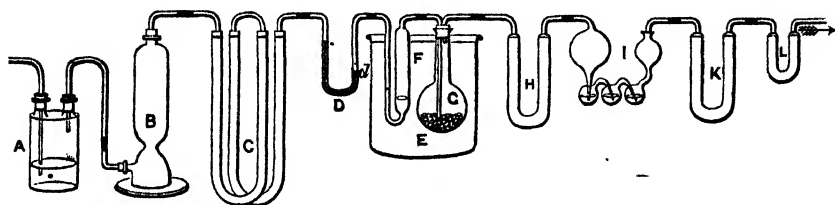


Fig. 2.

A. Bottle containing strong potash-solution.

B. Cylinder filled with soda-lime.

C. Series of calcium chloride tubes.

This part of the apparatus is for perfectly purifying and drying the air.

D. A small mercury valve. The bend of the tube is made of a piece of capillary tubing blown on to a piece of ordinary quill-tubing, in such a way that it forms a small cup at *d*; in this cup a small globule of mercury is placed. When no air is being aspirated through the apparatus, the globule of mercury falls into the cup, and closes the orifice of the capillary tube, cutting off all communication between the two parts of the apparatus. The mercury valve is a very necessary contrivance, for without it the calcium chloride in the tubes C would absorb moisture from the tube F, and vitiate the results.

E. A copper bath, filled with water, and provided with a cover to exclude the light. The temperature of the bath is regulated in cold weather by means of a thermostat.

F. A small tube containing about 1 to 1.5 c.c. of distilled water, the use of which is to saturate the dry air with moisture before it enters the germination-flask.

G. The germination-flask; capacity about 100 c.c. To grow about 15 grams of steeped barley.

H. Chloride of calcium tube.

I. Potash-bulbs, charged with KHO solution.

K. Tube half filled with soda-lime, and half with calcium chloride.

L. Guard-tube, to which is attached the aspirator. Great care is required in fitting up the apparatus to insure its being air-tight. When connected up, a few blank experiments ought to be made to test its efficiency. Supposing it to be in good working order, then if about 3,000 c.c. or so of air are aspirated, it should be found, by weighing F, H, I, and K, before and after the experiment, that H has

gained what F has lost, and that K has gained what I has lost, within a milligram.

In cold weather the greatest care must be taken to prevent the condensation of water in the tubes from F and G. A good plan is to cover the top of the water-bath with a conical hood of brown paper, in which a current of slightly warmed air is kept circulating. The method of using the apparatus is as follows:—

A weighed quantity of steeped barley is placed in the germination-flask. Then F, G, H, I, and K, are carefully weighed. The different parts are connected together, and air is aspirated at frequent intervals for 24 hours, or as long as may be desired; at the end of that time the same parts are again weighed. The gain of I and K together give the amount of carbonic anhydride disengaged, from which may be calculated the weight of carbon oxidised; and this is, of course, the weight of carbon lost by the barley in the flask G.

The tube H in most cases gains exactly the amount of moisture which F loses, but sometimes it gains more and sometimes less. It is clear that the extra moisture must either come from, or be retained by, the flask G, and therefore a correction must be applied; in the first case, the difference in weight between H and F must be deducted from, and in the second case added to, the total loss by weight of the flask G, so that the actual loss of weight through chemical change, which is sustained by the barley, can be ascertained. By following out this plan it is found that the germinating barley seldom loses as much in weight as is represented by the carbon oxidised (as calculated from the amount of CO_2 evolved), and since we know that nitrogen is not absorbed, the cause of this difference can only be the absorption of oxygen. It follows that if the loss of weight of the barley be deducted from the weight of carbon oxidised, the residuary weight represents the quantity of oxygen absorbed and retained. The following table shows some of the results obtained:—

Days of 24 hours.	Experiment 1. Bedfordshire barley, dried at 90° F. 10·5185 grams.			Experiment 2. Bedfordshire barley, dried at 90° F. 10·4927 grams.		
	Carbon oxidised.	Loss of weight of barley.	Oxygen absorbed and retained.	Carbon oxidised.	Loss of weight of barley.	Oxygen absorbed and retained.
	gram.	gram.	gram.	gram.	gram.	gram.
1	0·0122	0·0079	0·0043	0·0062	0·0023	0·0039
2	0·0212	0·0135	0·0077	0·0207	0·0147	0·0060
3	0·0256	0·0181	0·0075	0·0266	0·0166	0·0100
4	0·0211	0·0149	0·0062	0·0229	0·0210	0·0019
5	0·0206	0·0158	0·0048	0·0196	0·0149	0·0047
6	0·0210	0·0140	0·0070	0·0226	0·0175	0·0051
7	0·0204	0·0152	0·0052	0·0240	0·0194	0·0046
8	0·0229	0·0153	0·0076	0·0222	0·0167	3·0055
9	0·0234	0·0186	0·0048	0·0231	0·0139	0·0092
10	0·0222	0·0144	0·0078	0·0239	0·0187	0·0052
11	0·0240	0·0203	0·0037	0·0243	0·0190	0·0053
	0·2346	0·1680	0·0666 = 46·4 c.c.	0·2361	0·1747	0·0614 = 42·8 c.c.

These two experiments are fair specimens of the results generally obtained. But it must be borne in mind that a fertile source of accidental error is always introduced where an apparatus, with so many caoutchouc connections, is employed; there are no fewer than 12 joints to be made as perfect as possible every time the apparatus is connected together. If (as in these experiments) the weighings are taken daily, the source of error referred to is much larger than if the weighings are taken once in every three or four days. Specimens of two experiments, conducted in the latter way, are given on page 656, and will be again referred to. It will be seen, on examining the table given above, that there is not a large preliminary absorption of oxygen before the carbonic anhydride begins to be produced; but that the oxygen required for this purpose is absorbed as it is required, in the same way as it is used by animals in respiration. It will also be seen that there is daily retained by the barley, a weight of oxygen equal to about one-third or one-fourth the weight of carbon oxidised. In some other experiments which I have made, I find that the proportion may be considerably increased, and the amount of oxygen absorbed and retained reduced almost to zero, if the air in which the barley is grown be allowed to become much contaminated with carbonic anhydride.

As to what becomes of the oxygen absorbed and retained, I hardly like to venture an opinion; I do not consider that it goes to the for-

mation of water, but rather that it is absorbed in the same way as by a saccharine wort, when, as shown by Pasteur, it combines with certain substances, and manifests its action by a deepening of the colour of the liquid. An oxidised wort of this kind, if fermented by yeast, loses the colour acquired by oxidation, probably owing to the removal of the oxygen absorbed. Now if this oxygen had formed water by its combination, it would be hardly possible for the ferment to have recovered it. Taking this into consideration, and the fact that the extra amount of oxygen absorbed by growing barley diminishes as the air in which it is grown becomes contaminated with carbonic anhydride, I am inclined to believe that this extra absorption has very little connection with the internal reaction by which the carbonic anhydride is produced.

In Experiment 1 (page 651) 0·2346 gram of carbon is oxidised to CO_2 ; to effect this, 0·5379 gram or 375·2 c.c. of oxygen are required. The oxygen absorbed and retained by the barley amounts to 46·4 c.c. The proportion between the oxygen retained and that excreted as CO_2 , is therefore $\frac{46\cdot4}{375\cdot2} = 1 : 8\cdot08$. In Experiment 2 (page 651) 0·2361 gram of carbon is oxidised to CO_2 ; to effect this 0·5407 gram or 377·1 c.c. of oxygen are required. The oxygen absorbed and retained by the barley is 42·8 c.c. The ratio between the retained oxygen and that excreted as CO_2 is therefore $\frac{42\cdot8}{377\cdot1} = 1 : 8\cdot81$

Days of 24 hours.	Experiment 1. Bedfordshire barley, dried at 90° F. 10·6629 grams.			Experiment 2. Bedfordshire barley, dried at 90° F. 10·6167 grams.		
	Carbon oxidised.	Weight lost by barley.	Oxygen absorbed and retained.	Carbon oxidised.	Weight lost by barley.	Oxygen absorbed and retained.
	gram.	gram.	gram.	gram.	gram.	gram.
1	—	—	—	—	—	—
2	—	—	—	—	—	—
3	—	—	—	—	—	—
4	0·0830	0·0729	0·0101	0·0836	0·0659	0·0177
5	—	—	—	—	—	—
6	—	—	—	—	—	—
7	—	—	—	—	—	—
8	0·1023	0·0738	0·0285	0·1105	0·0763	0·0342
9	—	—	—	—	—	—
10	—	—	—	—	—	—
11	0·0680	0·0536	0·0144	0·0697	0·0510	0·0187
	0·2533	0·2003	0·0530 = 37·0 c.c.	0·2638	0·1932	0·0706 = 49·2 c.c.

I will now give the results of the two experiments (p. 656), mentioned on page 651, in both of which the same conditions of temperature and moisture were maintained as nearly as possible.

The amount of oxygen retained by the barley in the second experiment is considerably greater than that in the first. This appears to bear out the idea, stated on page 652, that there is probably no connection between the reaction by which the oxygen is retained, and that which gives rise to the carbonic anhydride. In Experiment 1, 0.2533 gram of carbon is oxidised to CO_2 . This requires 0.6754 gram or 464.1 c.c. of oxygen. The oxygen retained by the barley is 37.0 c.c. The ratio between the retained oxygen and that excreted as CO_2 is $\frac{37.0}{464.1}$ or 1 : 12.5. In Experiment 2, 0.2638 gram of carbon is oxidised to CO_2 . This requires 0.7043 gram or 491.3 c.c. of oxygen. The oxygen retained by the barley amounts to 49.2 c.c. The ratio between the retained oxygen and that excreted as CO_2 is therefore $\frac{49.2}{491.1} = 1 : 9.98$.

Many other experiments bear out the fact that there is no constant ratio between the oxygen required to produce the carbonic anhydride and that retained by the barley.

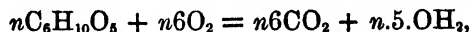
4. *The Production or Liberation of Water, by Internal Chemical Change, during Germination.*

As water is often one of the products of the complete or incomplete oxidation of organic compounds, especially where carbonic anhydride happens to be one of the bodies formed, it appeared to me to be highly probable that either a formation or a liberation of water accompanies the production of carbonic anhydride during the germination of barley. The *formation* of water may be illustrated by the complete combustion of a hydrocarbon, thus, $\text{CH}_4 + 2\text{O}_2 = \text{CO}_2 + 2\text{OH}_2$; and the *liberation* of water by the complete oxidation of a carbohydrate, thus,* $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{OH}_2$. The fact that a certain amount of water is formed, was suggested by Schlossberger (*Organische Chemie*, 120, 1857) as mentioned by Mulder in his *De la Bière*, p. 103: "Schlossberger, d'autre part, dit que, dans la germination, les semences ne deviennent relativement pas plus pauvres, mais qu'elles deviennent au contraire plus riches en carbone, et qu'il se dégagé, pendant la germination, une quantité bien plus grande d'hydrogène sous forme d'eau. Cette hypothèse n'est du reste appuyée de l'indication d'aucune expérience." It seems to be inferred here by Schlossberger that hydrogen is actually oxidised to form water, which hardly seems to be borne out by experiment. Later on in the same book the following passage occurs

* Empirical formula of a glucose.

(p. 120), relating to the disappearance of a portion of the carbohydrates during germination:—"Nous voyons qu'il y a eu une diminution, qui est de 82.2 à 81.0 = 1.2 : il y a donc diminution, et cette diminution est la conséquence de ce que l'on devrait désigner à présent sous le nom de 'respiration de la semence pendant la germination,' et qui consiste en une absorption d'oxygène et une production simultanée d'acide carbonique et d'eau, provenant, d'une oxydation d'une partie de l'amidon qui s'était transformé d'abord en dextrine, puis en sucre." This passage seems to me to be much nearer the truth. Supposing a part of the carbohydrates to be completely oxidised, there would be liberated a certain definite amount of water for every definite quantity of carbon oxidised. Of course the ratio of the water liberated to the carbon oxidised would vary with the nature of the carbohydrate split up.

In the case of a starch, the reaction would be as follows:—



or 5 molecules of water would be liberated for every 6 atoms of carbon oxidised to CO_2 . In the case of a glucose the equation would be, $C_6H_{12}O_6 + 6O_2 = 6CO_2 + 6OH_2$, or 1 mol. of water liberated for each atom of carbon oxidised.

In the case of a saccharose the equation is $C_{12}H_{22}O_{11} + 12O_2 = 12CO_2 + 11OH_2$, or 11 mols. of water liberated for every 12 atoms of carbon oxidised.

It was found in these experiments that there is more water in the barley after germination than before. There can be no doubt that it is not *formed* directly, since the amount of oxygen absorbed by the barley, during germination, is totally inadequate for the production of so large a quantity; it must therefore be *liberated*.

The amount of water liberated, during germination, was determined indirectly, in the same way that the amount of oxygen in a carbohydrate is estimated, by determining directly the amount of carbon and hydrogen, in a known weight of the substance, and subtracting the sum of the weight of these two elements from the weight of the carbohydrate employed, to find the weight of the oxygen.

It is perfectly evident that if a certain weight of barley be germinated and dried, the weight of the dry malt (including the rootlet) plus the weight of all the known losses which barley suffers during the process, ought to be equal to the weight of the barley before germination. It is found by experiment, however, that these two weights do not balance one another. The weight of malt (together with the rootlet) plus the weight of the known losses suffered during the germinating process, always falls considerably short of the weight of the barley employed. This difference, exclusive of experimental errors, can be

due only to the liberation of water, during germination, and its subsequent volatilisation in the drying of the malt.

It must be remembered that by estimating the liberated water in this way, any error in estimating the malt produced, or the amount of the losses suffered by the barley, must fall on the number representing the water liberated. Taking this into consideration, one can hardly expect perfectly concordant results, and indeed, the nature of the experiments will hardly allow of it, however great the precautions taken may be.

The losses sustained by barley during the process of being made into perfectly dry malt, are four in number. 1. The loss due to substances removed by the steep-water. 2. The loss during the growth of the corn, which, as has been previously pointed out, is rather less than the weight of the carbon oxidised. 3. The loss due to the removal of the water originally contained in the barley. 4. The loss caused by the removal of the water liberated during germination. The loss due to volatile matter is extremely small, and may be safely neglected.

The loss during steep is estimated by carefully evaporating the steep-water, and drying at 100° C. in a weighed dish. The results obtained are very concordant. The residue is of a light brownish colour.

The loss of weight during the growth of the barley, as well as the amount of carbon oxidised, is determined in an apparatus similar to that sketched in Fig. 2 (page 649). The loss due to original water in the barley is ascertained by estimating it in a separate sample of the same barley. The method of estimating the loss due to liberated water has just been explained. The total amount of malt and rootlet produced is found by estimating the weight in a perfectly dry state.

A few words are here necessary concerning the drying of the barley and malt. The ordinary method of drying in a current of dry air at 100° C. cannot be employed without introducing two rather serious inconveniences; the first of which is that when powdered barley or malt is so treated, the oxygen of the air acts upon it in such a way that there is an easily weighable quantity of carbonic anhydride formed, but considerably more so in the case of malt, than in that of barley. The second inconvenience is, that if either of these substances be kept in a current of dry air at 100° C., they do not cease to lose weight to a very marked extent, even after the lapse of long periods (four or five days, for instance). By making use of a current of dry CO_2 , the first inconvenience is done away with, but not the last. There is, besides, a disadvantage attending the use of CO_2 , namely, that the malt, and probably also the barley, when allowed to cool in a current of this gas, occludes at least its own volume of that gas; and when a moderate quantity, say one or two grams, is being operated upon, the

amount of CO_2 absorbed easily affects the weighings. I may mention here, though it has no particular bearing on the subject, that powdered malt, when kept in the vacuum of a Sprengel's air-pump, at a temperature of about 100°C ., very slowly evolves CO_2 in small quantity for two or three days at least.

The method I finally adopted to determine the water in the barley and malt, is as follows :—

The substances were both reduced to as fine a state of division as possible, and a portion of the sample, 1.5 to 2 grams, placed in a tube (Fig. 3). The air was exhausted, and pure dry nitrogen gas admitted. The tube was gradually raised (in a salt and water bath) to a temperature of 100° to 105°C . A vacuum was again produced and maintained for five minutes, when nitrogen was introduced as before. This operation had to be repeated 32 times (the vacuum being maintained for five minutes each time) before the tube and its contents ceased to lose weight. A calcium chloride tube was placed between the tube containing the powdered barley or malt and the air-pump, in order to check the

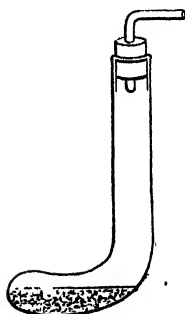


Fig. 3.

result. The gain of the calcium chloride tube always approximated very closely to the loss suffered by the tube containing the powdered barley or malt.

I give below the results of five experiments, relating to the liberation of water during germination, which were made with the greatest care in every detail.

They were all performed on the same kind of barley, viz., Bedfordshire, harvested in 1878, and partially dried at 90°F . In each sample used, every corn was carefully selected, so as to insure similarity in all cases, as far as possible, though the conditions of temperature and moisture under which they were grown might vary somewhat.

	grams.	grams.
I. Weight of barley employed	—	10.5185
Dry malt and rootlet obtained	8.7558	—
Loss during steep	0.0685	—
Loss during actual growth	0.1680	—
Loss due to original water in barley	1.4117	—
Sum	10.1340	—
Difference = OH_2 liberated during growth ..	—	0.3845

Weight of carbon oxidised = 0.2346 gram.

Carbon. OH_2 liberated.

0.2346 : 0.3845 :: 12 : 19.67.

	grams.	grams.
II. Weight of barley employed	—	10·4927
Dry malt and rootlet obtained.....	8·7615	—
Loss during steep	0·0880	—
Loss during actual growth	0·1747	—
Loss due to original water in barley	1·1389	—
Sum.....	10·1581	—
Difference = OH ₂ liberated during growth ..	—	0·3346

Weight of carbon oxidised = 0·2361 gram.

Carbon. OH₂ liberated.

0·2316 : 0·3346 :: 12 : 17·01.

	grams.	grams.
III. Weight of barley employed	—	10·4361
Dry malt and rootlet obtained.....	8·6797	—
Loss during steep	0·0671	—
Loss during actual growth	0·2088	—
Loss due to original water in barley	1·1327	—
Sum.....	10·0883	—
Difference = OH ₂ liberated during growth ..	—	0·3478

Weight of carbon oxidised = 0·2417 gram.

Carbon. OH₂ liberated.

0·2417 : 0·3478 :: 12 : 17·28.

	grams.	grams.
IV. Weight of barley employed	—	10·6629
Dry malt and rootlet obtained	8·9050	—
Loss during steep	0·0612	—
Loss during actual growth	0·2003	—
Loss due to original water in barley	1·1573	—
Sum.....	10·3238	—
Difference = OH ₂ liberated during growth ..	—	0·3391

Weight of carbon oxidised = 0·2533 gram.

Carbon. OH₂ liberated.

0·2533 : 0·3391 :: 12 : 16·05.

	grams.	grams.
V. Weight of barley employed	—	10·6167
Dry malt and rootlet obtained.....	8·7491	—
Loss during steep	0·0516	—
Loss during actual growth	0·1932	—
Loss due to original water in barley	1·1523	—
Sum.....	10·1462	—
Difference = OH ₂ liberated during growth ..	—	0·4707

Weight of carbon oxidised = 0·2638 gram.

Carbon. OH₂ liberated.

0·2638 : 0·4707 :: 12 : 21·4.

The ratio between the carbon oxidised to CO_2 and the water liberated during germination, in the five foregoing experiments, is as follows:—

No. 1.....	12 C	:	19.67 OH_2
„ 2.....	12 „	:	17.01 „
„ 3.....	12 „	:	17.28 „
„ 4.....	12 „	:	16.05 „
„ 5.....	12 „	:	21.40 „

The mean ratio is 12 C:18.28 OH_2 . According to this last, for every atom of carbon ($\text{C} = 12$) oxidised to CO_2 , during germination, there is liberated 1 mol. of water ($\text{OH}_2 = 18$). This agrees very closely with the equation representing the complete oxidation of a glucose, thus: $\text{CH}_2\text{O} + \text{O}_2 = \text{CO}_2 + \text{OH}_2$, CH_2O being the empirical formula of a glucose.

LVII.—On Metallic Compounds containing Bivalent Hydrocarbon-radicals. Part I.

By J. SAKURAI, Clothworker Scholar, University College, London.

WITH the view of isolating metallic combinations of olefiant gas, Wanklyn and Von Than (*Jour. Chem. Soc.*, 12, 258) studied the action of mercury and zinc upon ethylene iodide; but they failed in obtaining even a trace of organo-metallic compounds. I repeated their experiments, not only with iodide and chloride of ethylene, but also with the bromide and the chloriodide, and under various conditions; but the results obtained are essentially the same as those described by the above-named chemists. Olefiant gas is given off in abundance, and metallic chloride, bromide, or iodide is formed at the same time. In the case of ethylene chloriodide with zinc, some other reactions take place, which I shall have occasion to describe in detail in a future communication.

It appeared probable that with methylene iodide, this decomposition into metallic iodide on the one hand, and the hydrocarbon on the other, would be impossible; or, at any rate, would not take place under such circumstances as those which, while easily allowing the ethylene-compound to decompose, are, at the same time, favourable for or essential to the formation of organo-metallic compounds.

This anticipation was realised. On leaving methylene iodide in contact with metallic mercury and some mercurous iodide in a sealed

tube, combination takes place, and in four or five days the contents of the tube are turned into a yellowish-white mass, which after some time assumes a red colour. One point of interest in the reaction consists in the part played by mercurous iodide. This, under the influence of light, decomposes into metallic mercury and mercuric iodide, the former entering into combination with methylene iodide, and the latter, taking up fresh mercury, reproduces mercurous iodide, ready for decomposition. On opening the tube, not a trace of gas is given off.

Chiefly two products are formed. One of these, when properly purified, is a white crystalline substance, insoluble in water, cold alcohol, ether, chloroform, ethyl iodide, or benzene. It is somewhat soluble in boiling alcohol, from which it crystallises out on cooling in perfectly white, slender needles. But by far the best solvent for it is methylene iodide, which when hot takes up a considerable quantity of the substance, and allows a part of it to crystallise out on cooling. From the mother-liquor, ether precipitates it almost completely in the form of fine crystals. The crystals melt at $108-109^{\circ}$ to a clear yellow liquid, in which state the compound remains up to a considerably higher temperature. On cooling, it solidifies to a yellow crystalline mass, and re-melts at the original temperature. On analysis, the following numbers were obtained:—

I. 0.2075 gram of the substance gave 0.1030 gram of mercuric sulphide;

II. 0.0910 gram of the substance gave 0.0455 gram of mercuric sulphide;

and 0.0910 gram of silver iodide.

Thus—

	Found.		
	I.	II.	Calculated for CH_2HgI_2 .
Mercury	42.790	43.100	42.735
Iodine	—	54.040	54.273

By heating with a solution of iodine in potassium iodide, the substance is decomposed into methylene iodide and mercuric iodide, which latter is held in solution by the iodide of potassium; and by using a known quantity of iodine in excess, and determining what is left after the reaction is completed, the amount of iodine taken up may be ascertained. It was found in this way that 100 parts by weight of the substance require 54.540 parts of iodine, which correspond with 42.935 parts of mercury, as the following figures show:—

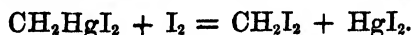
I. 0.2075 gram of the substance required 0.11332 gram of iodine.

II. 0.3220 " " " 0.17540 "

Or

	I.	II.	Mean.
Iodine needed per 100 of the substance. .	54.61	54.47	54.540
Mercury calculated from iodine needed. .	43.00	42.87	42.935

If the substance contains in its molecule nothing but a molecule of methylene iodide and an atom of mercury, it ought to require, for the completion of the reaction, *i.e.*, for the production of methylene iodide and mercuric iodide, just as much iodine as it contains, thus:—



Now, the direct determinations of mercury and iodine, as previously recorded, confirm this view beyond any reasonable doubt.

It may perhaps be desirable to describe here briefly the method of analysis employed. Taking the special case (No. I), 0.2075 gram of the substance was heated with 0.315 gram of pure iodine dissolved in pure potassium iodide, in a sealed tube at 100° C. for about half an hour. When cold, the tube was opened, and its contents carefully washed off into a beaker. A standard solution of sodium thiosulphate (1 c.c. = 0.01176 gram of iodine) was then run in; 17.15 c.c. of it were required, which correspond to 0.20168 gram of iodine. It is evident that 0.315—0.20168 = 0.11332 gram of iodine was used up by 0.2075 gram of the substance, or 54.61 per 100. The liquid in the beaker was passed through a filter, the latter carefully washed, and to the filtrate a few drops of ammonia were added, and then a clear solution of ammonium sulphide in excess. The precipitate was filtered, washed, dried at 100° C., and weighed. 0.103 gram of mercuric sulphide was obtained = 42.79 per cent. mercury, that calculated from the amount of iodine needed being 43.00 per cent. Iodine was determined by heating the substance with silver nitrate and hydric nitrate in a sealed tube, and weighing it as iodide of silver. From the same portion, mercury was determined by precipitating it as sulphide, after the excess of silver was removed.

Bromine and chlorine act upon the body similarly to iodine, forming methylene and mercuric bromide in one case, and methylene and mercuric chloride in the other, iodine being set free in both cases.

The simplest, and indeed the most reasonable constitutional formula that can be assigned to this new body, which may be termed *mono-mercuric methylene iodide*, is $\text{I}(\text{CH}_2)\text{HgI}$, the bivalent radical methylene $(\text{CH}_2)''$ combining to the extent of half of its power with iodine, on the one hand, and to the same extent on the other, with HgI , which plays the part of a monatomic radical. The novelty of the compound is revealed in the fact just stated, inasmuch as all the so-called organo-metallic bodies hitherto known are characterised by the monatomic nature of the alcohol-radicals which they contain, *viz.*, methyl, ethyl, amyl, and allyl. The relation between these two

classes of compounds is rendered evident by the comparison of their formulæ—



It has already been stated that two products are formed by the action of mercury upon methylene iodide. The second compound is a yellowish-white body, for which no solvent has yet been found, and which, therefore, has not yet been obtained in the pure state. It was, however, analysed, and from the results, as well as from some of its reactions, there is reason to believe that the body is dimeric mercuric methylene iodide, $\text{CH}_2(\text{HgI})_2$. It is, however, now under investigation.

When alcohol is used together with methylene iodide in the production of these bodies, some different products are formed, one of which is mercuric iodomethide. How it is formed, and what are its collateral products, will be communicated in a future paper.

I had occasion to try the action of methylene iodide upon sodium-amalgam in presence of acetic ether. The results of this experiment, as well as those of the action of zinc and other metals upon methylene iodide, which I am now studying, will, I hope, be shortly communicated. If the zinc-compound be successfully isolated, it cannot fail to be of great interest, and will, I hope, be found of service in building up bodies of the homologous series, where the consecutive members differ by CH_2 . We may thus be able to synthesise higher alcohols by a comparatively simple process.

I cannot conclude these notes without expressing my best thanks to Professor Williamson, under whose masterly guidance these experiments have been performed.

LVIII.—On the Action of Benzaldehyde on Phenanthraquinone, both alone and in presence of Ammonia.

By FRANCIS R. JAPP, M.A., Ph.D., Demonstrator in the Chemical Research Laboratory, Science Schools, South Kensington, and EDGAR WILCOCK.

PART I.—Action of Benzaldehyde on Phenanthraquinone.

WHEN phenanthraquinone is heated in a sealed tube with one and a half times its weight of benzaldehyde, free from hydrocyanic acid, at a temperature of between 250° and 270° for about six hours, the

contents of the tube solidify on cooling to a pale brown mass. If pure aldehyde has been employed there is no pressure in the tube on opening. By digesting with hot alcohol, a quantity of colouring matter is removed, and a grey pulverulent substance remains. This substance is purified as far as possible by repeated digestion with hot alcohol, in which it is almost insoluble, and is then recrystallised several times from boiling coal-tar oil (b. p. 150—170°), from which solution it is deposited in microscopic rosettes of plates, the colouring matter remaining in the mother-liquor. Finally it is crystallised from boiling bisulphide of carbon, and is thus obtained in small, colourless, well-formed, rectangular plates, of perfectly homogeneous character. Combustion yielded the following results:—

I. 0.1621 gram gave 0.5432 gram carbonic anhydride and 0.0748 gram water.

II. 0.1766 gram gave 0.5905 gram carbonic anhydride and 0.0821 gram water.

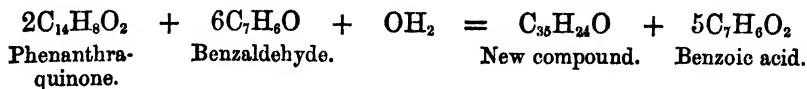
III. 0.1806 gram gave 0.6040 gram carbonic anhydride and 0.0884 gram water.

These results point to the formula $C_{35}H_{24}O$.

	Calculated.		Found.			Mean.
			I.	II.	III.	
$C_{35} \dots$	420	91.30	91.39	91.19	91.21	91.26
$H_{24} \dots$	24	5.22	5.12	5.16	5.33	5.20
$O \dots$	16	3.48	(3.49)	(3.65)	(3.46)	(3.54)
	460	100.00	100.00	100.00	100.00	100.00

Analyses I and II were made with the same preparation of substance; in III, a different preparation was employed. The first preparation fused at 329.5°, the second at 325°. The higher melting point is probably nearer the truth, as in the second case the substance had a faint pinkish tinge.

The formation of the compound $C_{35}H_{24}O$ may be explained by the equation—



The product of the reaction was in fact found to contain large quantities of benzoic acid. Whether the small quantity of water (not quite 3 per cent. of the benzaldehyde) which is required by the above equation was contained in the benzaldehyde, or whether a molecule of benzoic anhydride is formed in the reaction, we must leave for the

present undecided; but some observations which we have made with phenanthraquinone and acetaldehyde favour the latter view.

The substance is not very readily soluble in any of the usual solvents; boiling benzene and its higher homologues, and bisulphide of carbon dissolve it most freely. The benzene solution deposits nearly the whole of the substance on cooling; cold bisulphide of carbon retains a larger quantity. Boiling alcohol takes up only traces; boiling glacial acetic acid dissolves it somewhat more readily.

The substance may be sublimed at a very high temperature, but a considerable portion undergoes decomposition.

Concentrated sulphuric acid does not act upon the substance in the cold, but, when heated to near its boiling point, dissolves it, forming a red liquid with a brown fluorescence. On boiling with the acid, the colour deepens, but no carbonisation takes place. If a small quantity of water is now added and the solution cooled, a red precipitate is formed, which dissolves in an excess of water, yielding a magenta-coloured liquid devoid of fluorescence.

The very great stability of the compound $C_{35}H_{24}O$ has proved a serious obstacle in the way of investigating its constitution. Of the numerous reactions which were tried, some of which are enumerated below, only two—oxidation with a mixture of potassium dichromate and sulphuric acid, and reduction by distillation with zinc-dust—can be said to have yielded any positive results.

Oxidation.—A portion of the substance, in the finely divided condition in which it is obtained by deposition from its solution in hot benzene, was boiled with an oxidising mixture of 1 part of potassium dichromate and $1\frac{1}{2}$ parts of sulphuric acid diluted with 3 times its volume of water. After boiling for about an hour, water was added to the contents of the flask, and the solid matter was filtered off. The latter, which was of an orange-yellow colour, was thoroughly washed on the filter with boiling water, the wash-water being added to the first filtrate, A. The solid portion was now digested with a warm concentrated solution of hydrogen-sodium sulphite, which dissolved everything except a little unoxidised substance. This was filtered off, and to the filtrate was added first dilute sulphuric acid, and then, in order to oxidise the dissolved sulphurous anhydride, potassium dichromate in excess. A precipitate of pure phenanthraquinone, fusing at 205.5° (m. p. of phenanthraquinone 205°) was thus obtained.

The filtrate A was now distilled with steam as long as the distillate showed an acid reaction. The distillate was then rendered slightly alkaline with sodium carbonate and evaporated to a small bulk. On acidifying with hydrochloric acid, a copious separation of benzoic acid took place. The acid sublimed in the characteristic plates, and fused at 121.5° .

In another oxidation experiment, in which the minute plates deposited from the solution in bisulphide of carbon were employed, the substance was so slowly attacked that the phenanthraquinone was oxidised as soon as formed, and only benzoic acid, along with a large quantity of unattacked substance, could be found.

The products of oxidation thus identified were, therefore, benzoic acid and phenanthraquinone.

Distillation with Zinc-dust.—2 grams of the substance were mixed with 10 times their weight of zinc-dust, and distilled from combustion-tubing, heating from the open end of the tube gradually backwards. The distillate, of which there was a good yield, solidified at once, and was only slightly coloured. It was crystallised from hot alcohol, from which it was deposited in colourless laminæ, fusing at 96°. It yielded a picric acid compound, crystallising from alcohol in orange needles, and fusing at 141°. The distillate consisted, therefore, of phenanthrene.

In order to ascertain whether any other hydrocarbon was formed at the same time, the above experiment was repeated with a larger quantity of substance (4 grams). The entire distillate was dissolved in hot alcohol, and a slight excess of picric acid was added. The solution solidified on cooling to a magma of needles which, when filtered from the mother-liquor and washed with cold alcohol, fused at 143°. The united mother-liquor and wash-alcohol, evaporated to a small bulk, deposited a fresh quantity of needles, slightly darker coloured, and fusing at 140°. The mother-liquor from this second yield was evaporated to dryness, and the slight residue was digested with hot dilute ammonia. Everything went into solution with the exception of a few minute globules of substance, which fused in the boiling liquid and solidified on cooling, thus behaving like phenanthrene. Practically, therefore, the whole of the hydrocarbon present had been converted into the picric acid compound of phenanthrene.

From the formation of benzoic acid in the oxidation of the substance, we had thought it possible that toluene might occur among the products of distillation with zinc-dust. The end of the distilling tube was therefore, during the above experiments, connected by an adapter with a receiver cooled by ice-water. The solid hydrocarbon collected in the cool portion of the tube; the other vapours passed on and were condensed in the receiver. We found nothing in the receiver, however, but moisture from the zinc-dust, together with traces of solid hydrocarbon. None of the homologues of benzene could be detected, even by their odour.

Phenanthrene was therefore, as far as could be judged, the sole product of the distillation with zinc-dust.

Action of Zinc-ethyl.—When the substance is treated with cold zinc-

ethyl, it does not evolve gas. *This shows the absence of hydroxylic hydrogen in the compound.**

It was also heated with zinc-ethyl in a sealed tube to 150° , but no action took place.

Experiments with Negative Result.—The action of the following reagents was tried :—

Zinc-dust in boiling acetic acid. No change.

Hydriodic acid and amorphous phosphorus at 200° . No change.

Concentrated hydrochloric acid at 250° . No change.

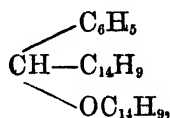
Boiling with alcoholic potash for two days. No change.

Fusion with potash. No action until a temperature was reached at which total decomposition occurred.

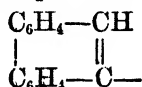
Distillation with soda-lime. Only a few drops of a tarry distillate, which did not invite further investigation, were obtained.

Aniline at 250° . The substance crystallised out unchanged.

Constitution of the Compound $C_{35}H_{24}O$.—Keeping in view the formation of the compound $C_{35}H_{24}O$ from phenanthraquinone and benzaldehyde, and the facts that it contains no hydroxyl and yields on oxidation phenanthraquinone and benzoic acid, the most probable constitutional formula seems to be the following :—



in which the phenanthryl groups have the constitution—

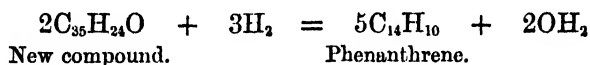


* This negative reaction—the non-evolution of gas from a substance when treated with cold zinc-ethyl—might be employed as a general test for the *absence of hydroxylic hydrogen and typical ammoniac hydrogen*. All compounds which contain hydrogen directly attached to oxygen or to nitrogen evolve ethylic hydride when treated with zinc-ethyl (Frankland, *Phil. Trans.*, 165, 259; *Proc. Roy. Soc.*, 8, 502). It is hardly necessary to observe that the test is a purely negative one, and that an evolution of gas is not the slightest proof of the presence of hydrogen in either of the above forms of combination.

The test is easily applied. The zinc-ethyl may be kept for the purpose in small thin sealed bulbs. One of these is dropped into a stout test-tube and then broken. It is not necessary to fill the tube with carbonic anhydride, as the zinc-ethyl will not inflame at the bottom of the narrow tube. The substance to be tested, previously thoroughly dried, is then introduced.

In this way, in the case of a complicated organic compound containing both oxygen and nitrogen, information may be gained in the course of a few minutes, which will lead to the exclusion of several competing and otherwise probable constitutional formulæ, and to a corresponding simplification of the question in hand (see further in present paper).

as contained in monobromphenanthrene and β -phenanthrene-carboxylic acid. The compound would therefore be a *phenanthrylic ether of phenyl-phenanthryl-carbinol*. This formula would involve a separation of carbon from carbon in the distillation with zinc-dust, in order that only phenanthrene might be formed in that process; but there is no way of arranging the various groups in the molecule which would avoid this difficulty. In the distillation with zinc-dust the group $C_6H_5-CH=$ might combine with another similar group, at the same time eliminating hydrogen, so as to form phenanthrene, as in Graebe's synthesis of this hydrocarbon from stilbene. Thus we might have—



to express the result of the distillation with zinc-dust.

The fact that no ketone was obtained on oxidation would be explained by the relatively greater ease with which the phenanthryl groups would be oxidised to phenanthraquinone, a process which would be attended with a disruption of the various constituent groups of the molecule.

As we do not, however, regard the above constitutional formula as more than a suggestion, we prefer to adopt provisionally a name for this compound by which its mode of formation rather than its constitution should be expressed. *Benzalquin of phenanthrene* would, we think, serve this purpose. Should the reaction prove to be of general application, a series of names embodying the names of both aldehyde and quinone might be constructed on this principle.

The investigation is to be extended to the mutual action of other aldehydes and quinones. In this way further light may perhaps be thrown on the nature of the compound above described.

PART II.—Action of Benzaldehyde on Phenanthraquinone in presence of Ammonia.

In some experiments which were undertaken with a view to ascertain the most suitable temperature for the formation of benzalquin of phenanthrene, on one occasion ordinary oil of bitter almonds, containing hydrocyanic acid, was employed. At the boiling point of the aldehyde the substances had no action upon each other, even when boiled together for five or six hours. At 200° in a sealed tube some action took place: the quinone did not crystallise out on cooling, but no definite product could be isolated. Heated for six hours to 220° , however, the contents of the tube solidified on cooling to a mass of needles. By digesting with hot alcohol, in which they were almost insoluble, they were freed from a considerable quantity of colouring

matter. The substance was then recrystallised from boiling benzene, from which it was deposited on cooling in tufts of fine silky needles of a pale straw colour. This colour could not be removed by crystallisation, but was nevertheless due to an impurity, for by sublimation perfectly colourless needles could be obtained.

At first it was thought that this substance had been formed from benzaldehyde and phenanthraquinone alone, and that the difference between this reaction and that in which the benzalquin of phenanthrene had been obtained was due to difference of temperature. But on attempting to prepare the substance from phenanthraquinone and pure benzaldehyde, not a trace of it was produced. A qualitative test then showed that it contained nitrogen. As the only possible explanation of this seemed to be that the hydrocyanic acid in the benzaldehyde had taken part in the reaction, some pure benzaldehyde (prepared from the double compound with hydrogen-sodium sulphite) was saturated with hydrocyanic acid, and the liquid thus obtained was heated with phenanthraquinone in a sealed tube to 220°. The result showed that the above supposition was correct, a fair yield of the new compound being obtained.

A considerable quantity of the substance prepared in this way was purified by repeated crystallisation from boiling benzene. After seven or eight crystallisations it fused constantly at 202°. It yielded the following results on analysis, two different preparations being employed:—

I. 0.1193 gram gave 0.3733 gram carbonic anhydride and 0.0508 gram water.

II. 0.1525 gram gave 0.4782 gram carbonic anhydride and 0.0664 gram water.

III. 0.2470 gram gave 0.7722 gram carbonic anhydride and 0.1045 gram water.

IV. 0.2694 gram gave 9.752 c.c. (corr. vol.) nitrogen at 0° and under 760° mm. pressure, corresponding to 0.01225 gram nitrogen.

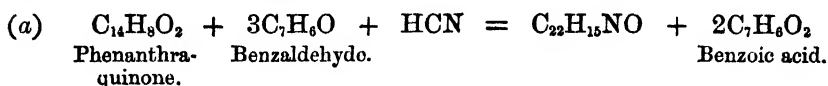
The percentages calculated from these figures agree with those required by the empirical formula $C_{22}H_{15}NO$, but are also very close to the numbers for the next lower homologue, $C_{21}H_{13}NO$.

	Calculated for $C_{21}H_{13}NO$.			Calculated for $C_{22}H_{15}NO$.	
C_{21}	252	85.43	C_{22}	264	85.43
H_{13}	13	4.41	H_{15}	15	4.85
N	14	4.74	N	14	4.53
O	16	5.42	O	16	5.19
	295	100.00		309	100.00

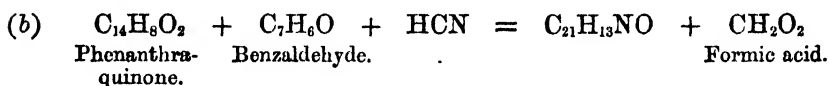
	Found.				Mean.
	I.	II.	III.	IV.	
C	85·34	85·52	85·26	—	85·37
H	4·73	4·83	4·70	—	4·75
N	—	—	—	4·54	4·54
O	—	—	—	—	(5·34)
					<hr/> 100·00

The following reasons decide conclusively in favour of the formula $C_{21}H_{13}NO$.

The formation of a compound of the formula, $C_{22}H_{15}NO$, could be explained by the equation—



On the other hand the equation—



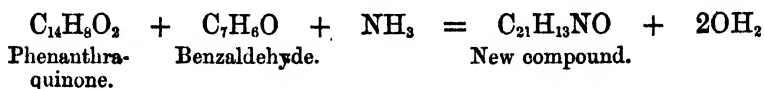
would account for the formation of the compound $C_{21}H_{13}NO$. The formic acid would of course, at the temperature at which the reaction takes place, be decomposed into carbonic oxide and water. As a fact, the tubes showed considerable pressure on opening. But no importance could be attached to a proof of the presence of carbonic oxide under the conditions of the above experiment. The hydrocyanic acid which was passed into the benzaldehyde was certainly not perfectly anhydrous, and aqueous hydrocyanic acid alone, when heated to 230° , would yield carbonic oxide.

According to equation (a) both the carbon and the nitrogen of the hydrocyanic acid are employed in forming the new compound; according to equation (b) only the nitrogen plays a part—the ammonia produced by the saponification of the hydrocyanic acid is the active agent.

In order to test the correctness of the latter supposition, phenanthraquinone with an excess of pure benzaldehyde was heated with strong aqueous ammonia in a sealed tube for six hours to 230 – 235° . In this way an almost quantitative yield of the new compound was obtained. The product, after washing with hot alcohol and crystallising from boiling benzene, consisted of perfectly colourless needles, fusing at 201° . There was no pressure in the tube on opening, and no resinous matter was formed. In another experiment in which the tube was heated for two hours to 200° , the yield was apparently equally

good. It is better to keep the temperature low, as the formation of benzalquin of phenanthrene is thus totally avoided.

The following equation expresses the reaction :—



During the greater part of the time which we spent in the investigation of this substance, we were under the erroneous impression that it possessed the formula $\text{C}_{22}\text{H}_{15}\text{NO}$, and it was not until we had completed the study of its reactions and had recognised the impossibility of constructing from this empirical formula a constitutional formula which should account for these reactions, that we were led to adopt the empirical formula $\text{C}_{21}\text{H}_{13}\text{NO}$, and to employ ammonia instead of hydrocyanic acid in the production of the substance. This was unfortunate, as the employment of hydrocyanic acid, besides being more troublesome, is accompanied by the formation of a large quantity of resinous matter—probably due to the action of formic acid or nascent carbonic oxide on the other substances present, thus reducing the yield and interfering with the purification of the product.

The following is a summary of the properties of this substance :— Crystallises in tufts of colourless silky needles, which under the microscope are seen to be flattened. Fuses at 202° . Sublimes and, in small quantities, may even be distilled without undergoing much decomposition. The boiling point lies far above the range of the thermometer. Readily soluble in boiling benzene and bisulphide of carbon, very sparingly soluble in alcohol and glacial acetic acid. Perfectly insoluble in water, but soluble in hot concentrated hydrochloric and dilute sulphuric acid, crystallising out unchanged on cooling, and thus displaying the properties of a weak base.

The substance is exceedingly stable, but does not resist the action of reagents so stubbornly as the benzalquin of phenanthrene.

Oxidation.—The substance was oxidised with the same mixture, and the products of oxidation were treated in the same manner as in the case of the benzalquin of phenanthrene (p. 663). Phenanthraquinone and benzoic acid were identified as products of oxidation, the former by its melting point (found $205\text{--}206^\circ$), and its solubility in hydrogen-sodium sulphite, the latter by its melting point (found $121\text{--}121.5^\circ$), and other characteristic properties.

Distillation with Zinc-dust.—This operation was performed as on p. 664. The distillate was dark-coloured and semi-solid, and smelt of benzonitrile. The quantity of this latter substance could not have been great, inasmuch as a strong odour of ammonia was given off during the whole of the distillation. The product was redistilled with

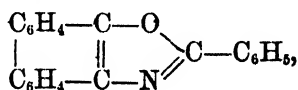
zinc-dust. This time the distillate was nearly colourless and solidified more thoroughly. The solid portion of the distillate was identified as phenanthrene. The hydrocarbon fused at 97·5—98°, the picric acid compound at 141°.

Action of Alcoholic Potash.—A portion of the substance was boiled with alcoholic potash for about a fortnight. During the whole of this time ammonia was slowly given off, nor had this evolution ceased when the operation was interrupted. After distilling off the alcohol, the contents of the flask were digested with water and filtered. In this way about half the substance was recovered unchanged. The filtrate was saturated with carbonic anhydride, which caused the separation of a quantity of resin, from which nothing definite could be isolated. This was filtered off. On adding hydrochloric acid to the liquid, an acid was precipitated, which after extraction from the solution with ether and purification by sublimation, was obtained in the characteristic laminæ of benzoic acid, and fused at 120·5°.

Action of Concentrated Hydrochloric Acid.—When heated with concentrated hydrochloric acid in a sealed tube to 200°, the substance was not acted upon, except that it dissolved in the acid, and crystallised out in tufts of needles on cooling. After heating to 250°, however, the tube was found to be filled with crystals of benzoic acid (m. p. 121·5°). The hydrochloric acid, filtered from the benzoic acid and evaporated to dryness, left a residue of ammonium chloride. There was also formed a resinous mass, from which sodium carbonate extracted a small quantity of benzoic acid, but which yielded no other definite product.

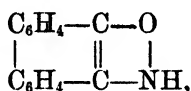
Action of Zinc-ethyl.—Treated with cold zinc-ethyl the substance did not evolve gas. The compound contains, therefore, neither hydroxylic, nor typical ammonic hydrogen (see p. 665). Zinc-ethyl, even at 150°, did not act on the substance.

Constitution of the Compound $C_{21}H_{13}NO$.—The constitutional formula—



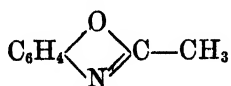
would account for all the reactions of this compound, and would also be in keeping with its mode of formation. A compound of this formula contains neither hydroxylic nor typical-ammonic hydrogen; it would yield on oxidation benzoic acid and phenanthraquinone; on distillation with zinc-dust, phenanthrene, and possibly benzonitrile, would be formed. When heated with concentrated hydrochloric acid it might be expected to take up the elements of water, and split up into benzoic acid, ammonia, and phenanthraquinol, which last would probably be resinated by the action of hydrochloric acid at that tem-

perature. The monethyl ether of phenanthraquinol, for example, undergoes resination when heated with concentrated hydrochloric acid, and it is in the highest degree probable that phenanthraquinol is first formed.) The separation of the nitrogen-atom as ammonia from the phenanthrylene-group in the action of hydrochloric acid may seem at first sight unlikely; but a precisely similar reaction takes place in the case of phenanthraquinonimide—

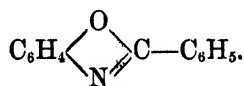


which, when treated with acids, takes up, even at ordinary temperatures, the elements of water, and is converted into phenanthraquinone and ammonia.

A compound of the above constitution would belong to the class of substances obtained by Ladenburg (*Ber.*, 9, 1524) by the action of anhydrides or chlorides of monobasic organic acids upon ortho-amidophenol. Two of these compounds will serve as examples—



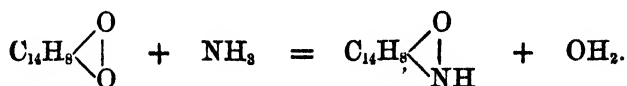
Ethenylamidophenyl.



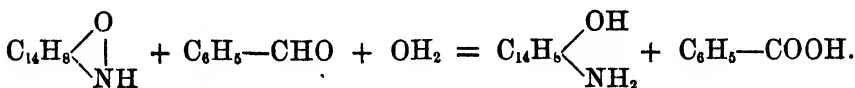
Benzenylamidophenol.

In the preparation of the first of these acetic anhydride, in that of the latter benzoic chloride, was employed. Adopting the above system of nomenclature the present compound would receive the name *benzenylamidophenanthrol*. A gradation is noticeable in the properties of these three compounds. Ethenylamidophenol is a weak base, salts of which can be obtained only with difficulty. The substitution of the more electronegative benzenyl for ethenyl so diminishes the basic power, that, though the substance dissolves in acids, it no longer forms definite salts, with the single exception of a chloroplatinate. Finally, in the case of the present compound, which may be regarded as derived from benzenylamidophenol by the substitution of the more negative phenanthrylene for phenylene, the only vestige of basic power is its solubility in acids at higher temperatures, from which solutions it crystallises unchanged on cooling.

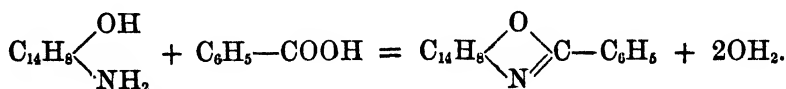
The reaction in which benzenylamidophenanthrol is produced may be interpreted in a way which renders it analogous to that discovered by Ladenburg. For this purpose it is necessary to suppose that the process takes place in three stages. In the first, phenanthraquinone and ammonia act upon each other, forming phenanthraquinonimide and water, as in the reaction described by Anschuetz and Schultz (*Ber.*, 10, 23)—



The phenanthraquinonimide is reduced by the benzaldehyde in presence of water to ortho-amidophenanthrol, benzoic acid being formed at the same time—

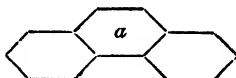


The ortho-amidophenanthrol and benzoic acid then undergo condensation, as in Ladenburg's reaction, yielding benzenylamidophenanthrol—



According to this interpretation the reaction ought not to be capable of extension to paraquinones, since, according to Ladenburg (*loc. cit.*), condensations of this class take place only in the ortho-series.

The existence of a compound of the constitution of benzenylamidophenanthrol, a strict analogue of benzenylamidophenol, adds one more to the number of facts which render it probable that the six carbon-atoms arranged in a closed chain (*a* in the annexed skeleton formula) in the central portion of the graphic formula of phenanthrene—



form a benzene nucleus (see also *Chem. Soc. J.*, 1880, 88).

LIX.—On a New Boro-copper Compound of the Formula B_2Cu_3 .

By R. SYDNEY MARSDEN, D.Sc., F.R.S.E., F.C.S.

THIS compound is formed by the direct union of amorphous boron and metallic copper, and is produced in the following manner:—Amorphous boron and metallic copper (in small lumps) are laid in alternate layers inside a Berlin porcelain crucible; this again is placed inside a graphite crucible, the intermediate space being filled with carbon (to keep out the oxygen and prevent it from uniting with

the boron), and the whole is heated for from three to four hours at a temperature considerably above the melting point of copper. It is then taken out and allowed to cool. On opening the crucible the compound is found in a single metallic lump at the bottom, and surrounded by a powder of greyish-white colour, consisting of nitride of boron, formed by the union of the nitrogen of the air with the superfluous amorphous boron. The metal, after being carefully cleaned from the adhering boron nitride, is found to possess the following physical properties.

1st. Its colour is (slightly reddish) yellow, resembling that of iron pyrites.

2nd. It is very hard, and will scratch bronze (of ordinary composition, such as the penny), though not steel or glass.

3rd. It is malleable but brittle.

4th. Its specific gravity is 8.116; that of copper being 8.921.

A qualitative analysis showed it to consist of copper, boron, and silica (the silica being there undoubtedly either as an impurity in the copper, or more probably owing to the fused metal having been in contact with the glaze of the porcelain crucible, and thus become mechanically mixed with it).

Quantitative analysis gave the following results:—

		I.		II.		Mean.
Copper =	79.75	79.76	79.75
Silica =	11.13	10.56	10.84
Boron =	9.12	9.68	9.41
		100.00		100.00		100.00

Hence, deducting the silica, which is present merely as an impurity, we find that the copper and boron are present in the proportion 79.75 to 9.41, agreeing very nearly with the formula B_2Cu_3 , which requires 79.75 copper to 9.22 boron.

The compound may be represented by the constitutional formula $Cu \equiv B - Cu - B \equiv Cu$.

The copper was estimated by Rose's method as subsulphide, which gave very accurate results.

The silica was estimated in the usual way as silica. I got rid of the boracic acid (which was formed by dissolving the compound in nitric acid) by continually diluting and evaporating it down in an evaporating basin on the water-bath. After it had been evaporated several times, it was put into the air-bath, and heated to 120° for half an hour, and then evaporated down again several times with water; in this way I found it possible to get rid completely of the boracic acid by volatilisation, and on diluting and filtering, to get the silica upon the filter in a pure state and weigh it.

The boron I did not consider necessary to estimate directly, but only by difference, the qualitative analysis showing the compound to consist only of copper, boron, and silica.

I may also mention that I tried to get similar compounds with lead and zinc, but was unable to do so; in neither case could I detect the presence of boron.

In conclusion I would wish to thank Dr. R. M. Morrison for the assistance he gave me in preparing this compound.

LX.—*Note on the Precipitation of Iron with Ammonium Succinate.*

By SYDNEY YOUNG, Student in the Chemical Laboratories of the Owens College.

No book dealing with a large number of experimental results can be expected to be absolutely free from mistake, and an error has crept even into "Fresenius' Quantitative Analysis," in the separation of so common a substance as iron.

In the seventh edition of that book, page 138, also in "Fresenius' Qualitative Analysis," edition 9, page 216, and in "Gmelin's Handbook," vol. x, page 126, it is stated that when a neutral solution of a ferric salt is precipitated by ammonium succinate, a certain amount of the precipitate is redissolved unless the operation be conducted in the cold, owing to the liberation of free succinic acid, which does not exert any solvent action in a cold and highly dilute solution, but dissolves the precipitate more readily when boiled.

Having on one occasion separated iron and zinc with ammonium succinate in a boiling solution with very good results, I made the following experiments to test the accuracy of the above statements.

A number of solutions of ferric chloride, neutralised as nearly as possible with ammonium carbonate, were first precipitated both hot and cold with ammonium succinate, the precipitates filtered off, and the filtrates tested for iron with potassium ferrocyanide. The filtrates from the hot liquid contained either no iron or the merest trace, whilst the cold filtrates contained a very small quantity, but distinctly more than the hot.

The action of concentrated and dilute succinic acid was next ascertained, with the following results:—

When the precipitate was formed in a boiling solution, and treated with either cold or hot succinic acid, or when formed in the cold and

boiled with succinic acid, either concentrated or dilute, the amount of iron dissolved was very small indeed, whilst, on the other hand, the solvent action of cold dilute succinic acid on a precipitate formed in the cold was much greater. Indeed, when the acid was concentrated, a considerable quantity of iron came into solution. In the last case the filtrate has a rather deep reddish-yellow colour, but on boiling it, the whole of the succinate of iron comes down again, the filtrate being quite colourless and clear, and containing but the merest trace of iron.

The quantities of iron redissolved in the above cases were then estimated. When the amount of iron was very small, Carnelley's colorimetric method was employed (*Chem. Soc. J.*, **28**, 285), while if the quantity was larger, the iron was reduced with zinc and pure sulphuric acid, and estimated by potassium permanganate. In each experiment a quantity of ferric chloride = 0.0403 gram of Fe was used.

1. The ferric chloride was precipitated in a boiling solution, and the iron in the filtrate estimated by Carnelley's method with the following result:—

Amount of iron =	(1) 0.00001 gram or less.
	(2) 0.00000
	(3) 0.00000
	(4) 0.00000 (the merest trace).
	(5) 0.00000
	(6) 0.00000
	(7) 0.00000
Mean	<u>0.0000014</u>

(2.) Precipitated in the cold the

amount of iron was	(1) 0.000070
	(2) 0.000020
	(3) 0.000020
	(4) 0.000010
	(5) 0.000010
	(6) 0.000010
	(7) 0.000015

Mean	<u>0.0000221</u>
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3. A precipitate was formed in the hot liquid, and was then treated with 0.05 gram succinic acid in 100 c.c. of water at the boiling point for an hour. The amount of iron in solution was found to be 0.00005 gram.

4. A precipitate was formed in the cold, and was treated with the

same quantity of cold succinic acid for an hour, when the quantity of iron in solution was found to be 0.00048.

5. The same quantity of ferric chloride was precipitated in the cold, filtered and washed, and the precipitate was treated with 0.05 gram succinic acid dissolved in 200 c.c. of water for three days, after which time 0.002785 gram of iron was found in solution.

6. A much more dilute acid was next employed, and was allowed to stand for five days, on account of the difficulty of filtering, the succinate of iron remaining in the solution in a state of very fine suspension. The filtrate was obtained quite clear, and contained 0.003515 gram of iron.

7. A precipitate formed at the boiling point ($= 0.027 \text{ Fe}$) was boiled for an hour with 50 c.c. of succinic acid containing 0.5 gram of acid. The filtrate was found to contain 0.00003 gram Fe.

8. Precipitated in the cold, then treated for an hour with cold acid as above, the amount of iron in solution was 0.0033 gram.

9. Precipitated in the cold and treated for two hours, the soluble iron amounted to 0.0069 gram.

The above results show clearly that the old tedious method of precipitating in the cold is quite unnecessary. A considerable amount of time is saved by using a boiling solution, because the precipitate then readily settles down, especially after boiling for two or three minutes, and is easily and quickly filtered and washed; moreover, the precipitate then never passes through the filter-paper, as not unfrequently happens when a cold solution is used.

In all the quantitative experiments pure succinic acid and ammonium succinate were used, obtained from Kahlbaum, of Berlin.

LXI.—*An Examination of Terpenes for Cymene by means of the Ultra-violet Spectrum.*

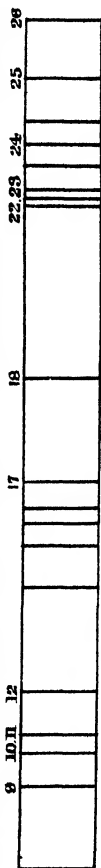
By W. N. HARTLEY, F.R.S.E., &c., Professor of Chemistry, Royal College of Science, Dublin.

In a paper by myself and Professor Huntington, an abstract of which appeared in the *Proceedings of the Royal Society*, 1879, it has been shown that cymene intercepts a narrow band of rays occupying a position extending a little to the right and left of the cadmium line No. 17, which line has a wave-length, according to M. Mascart's measurement, of 2743.4. A wide absorption-band occurs between the 17th and 18th cadmium lines, the wave-length of the latter is 2574.2.

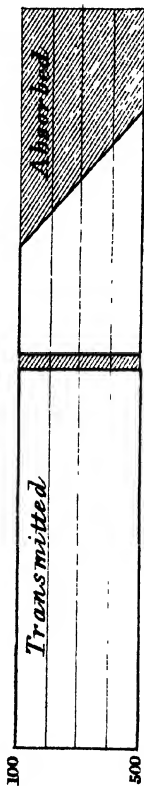
It was shown that this broad band of absorption is not entirely

Ordinates = the
volumes of liquid
containing 1 volume
of the terpenes.

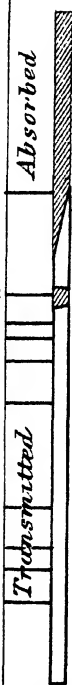
Numbers indicating the position of Cadmium lines of known wave lengths



ORANGE OIL



FRENCH TURPENTINE



RUSSIAN TURPENTINE

Ordinates = the
volumes of liquid
containing 1 volume
of the terpenes.

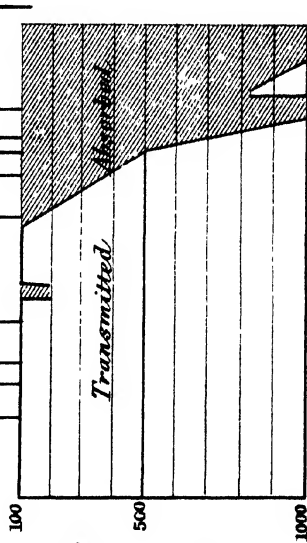


DIAGRAM 2.
Shewing the effect of adding
1 per cent by volume of
cymene to certain terpenes.
The absorption band seen at
the cadmium line No 17
is due to cymene



Numbers indicating the position of Cadmium lines of known wave lengths.

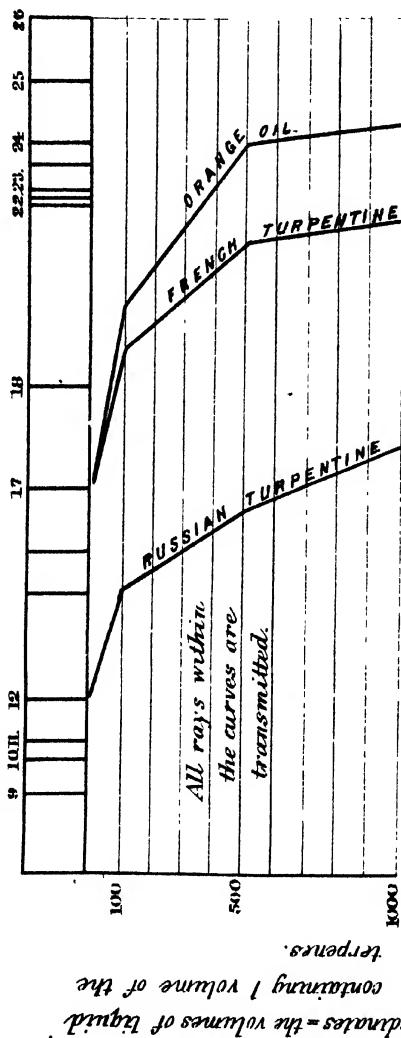


DIAGRAM 1.

Three terpenes examined for cymene.

None of the absorption bands characteristic of cymene are visible in solutions of various strengths.

obliterated by diluting the cymene with 5,000 volumes of alcohol if a layer of liquid 15 mm. in thickness be examined.

It was, therefore, easy to ascertain the presence of cymene in certain essential oils, such as the hydrocarbons of thyme, lemon, nutmeg and caraway, and in certain cases there was no difficulty in ascertaining the proportion present in the oils, for it was proved by us that pure terpenes transmit continuous spectra.

About a year ago I received three specimens called orange oil, French turpentine, and Russian turpentine from Dr. Armstrong, with a request that I would examine them and inform him of the amount of cymene they each contained. Photographs were taken of these oils, undiluted and in various states of dilution with alcohol. As in no case was there any indication of absorption-bands, I arrived at the conclusion that the orange oil and French turpentine contained no cymene, but that the Russian oil which was least diatonic and required a large amount of dilution, namely, to 800 times its original volume, might possibly contain a quantity under 4 per cent. cymene.

This conclusion did not agree with that of Dr. Armstrong, who had inferred from his own experiments that all the oils contained cymene, and the proportions in the French and Russian turpentines he estimated as amounting to 4 and 8 per cent. respectively.

The evidence I relied on was the uninterrupted transmission of all rays of the spectrum to a little beyond the line Cd 17, when the French and orange oils were examined without dilution, and a complete transmission of rays more refrangible than line Cd 18 when the liquids were diluted with alcohol to 100 volumes, while in the case of the less diatonic Russian oil, a dilution to 800 times its original volume was necessary to transmit rays more refrangible than line 17 Cd. (See Diagram 1.)

My removal from London to Dublin interrupted my experiments, but I have recently resumed work on the subject, and taken spectrum photographs of various dilute solutions of cymene, which show distinctly the absorption band at 17 Cd when the liquid contains only $\frac{1}{100,000}$ th and $\frac{1}{20,000}$ th of its volume of cymene; there are faint indications even when $\frac{1}{30,000}$ th is present.

It is evident therefore that the French and orange oils do not contain even $\frac{1}{20,000}$ th of their volume of cymene, while it is possible that the Russian turpentine which it is necessary to dilute to 800 times its original volume before the line 17 Cd is transmitted, may contain $\frac{1}{25}$ th its volume. In order to test this more effectually, I instructed Mr. W. E. Adeney, a student in the Royal College of Science, to take photographs of the three oils after $\frac{1}{100}$ th volume of cymene had been added, and this having been accomplished, Diagram 2 was drawn from the resulting photographs.

I conclude, therefore, that the cymene separated by Dr. Armstrong from the three oils was formed by the chemical treatment they were subjected to in order to effect such separation.

Drs. Armstrong and Tilden in a communication published in the Chemical Society's Transactions last November ("On the Action of Sulphuric Acid on the Hydrocarbons of the Formula $C_{10}H_{16}$ "), make the following statement:—"So-called terebene, in fact, does not exist, the substance described under this name being merely impure optically inactive camphene; and in the said product it is associated with terpine, the optically inactive isomeride of the terpenes which boils at about 178° , and also with cymene and a paraffin-like hydrocarbon of the formula $C_{10}H_{20}$."

Terebene prepared by Dr. Tilden from American turpentine by precipitation with sulphuric acid, optically inactive, boiling at 156° , was examined by me. It contained not the slightest trace of cymene, and I have little doubt that in this case the cymene was produced by the action of the sulphuric acid on the camphene.

LXII.—CONTRIBUTIONS FROM THE LABORATORY OF GONVILLE AND CAIUS COLLEGE, CAMBRIDGE.

N^o VI. *On Essential Oil of Sage.*

By M. M. PATTISON MUIR, M.A., F.R.S.E., Caius Prælector in Chemistry.

Two papers have already been published by me, in conjunction with Sigiura, on "Essential Oil of Sage" (see *Phil. Mag.*, Nov., 1877, and this *Journal*, 1878, *Proc.*, 292). The present paper contains an account of investigations made with the view of supplementing the information detailed in the papers referred to, and at the same time of giving a general account of essential oil of sage, so far as the facts gained enable such an account to be given.

1. The sage plant grows wild in quantity in the south of Europe, especially in Dalmatia, in parts of Italy, and in the department of the Alpes Maritimes in France. The plant is also cultivated in the neighbourhood of Grasse (Alpes Maritimes), near Leipzig, and in Thuringia. The plant is cut in the autumn and placed at once in stills along with water, the distillate is returned to the stills, and this process is repeated several times in succession. The Italian wild sage yields from

1 to 1.25 per cent. of oil, the Dalmatian and that cultivated around Leipzig about 0.5 per cent., while from the French plant only about 0.3 per cent. of oil is obtained.

I have had a quantity of the leaves of the English sage plant distilled for me by Messrs. Wright, Layman and Umney, but the yield of oil amounted only to 0.07 per cent. The oil obtained from the French plant is of a pale-yellow colour, that distilled at Leipzig is reddish-brown, sometimes inclining to a greenish shade. The smell of the French oil is sharper, and at the same time more sickly than that of the German.

Two samples of English oil were specially distilled for me; that distilled in summer was yellow-brown to dark-brown, whilst that distilled in winter had a distinctly green shade.*

The composition of the English oil was somewhat different from that of the oil distilled at Leipzig.

2. The oil with which I worked was obtained through Messrs. Wright, Layman and Umney; it was distilled by Messrs. Sacchse of Leipzig in the summer of 1877.

In previous papers (*loc. cit.*) it has been shown that the main constituents of sage oil are—1. Two hydrocarbons, each having the formula $C_{10}H_{16}$, boiling at about 156° and 167° respectively. 2. An oxidised compound, *salviol*, probably $C_{10}H_{16}O$, boiling at about 200° . 3. A camphor, $C_{10}H_{16}O$. 4. Probably a few per cents. of cymene. And 5. In the oil distilled from the leaves of English grown sage, a hydrocarbon boiling at about 260° and having the formula $C_{15}H_{24}$.

3. The results obtained by the distillation of sage oil since the date of these papers require that certain modifications be made in the preceding statement.

That specimen of sage oil which was employed in the experiments described in *Phil. Mag.*, Nov., 1877, was of unknown age and origin; it was comparatively rich in camphor, contained very small quantities of the oxidised liquid constituent, *salviol*, moderate quantities of the $C_{10}H_{16}$ hydrocarbons, and a small quantity of what was described as "a dark-brown liquid with distinct fluorescence," boiling about 240° . This last-named liquid undoubtedly contained *cedrene*, $C_{15}H_{24}$.

The sample of oil examined in 1877–78 (this *Journal*, *loc. cit.*) was of German manufacture, and had not been distilled more than three months before the time when it was examined. It yielded moderate quantities of *salviol*, very little camphor, considerable quantities of the $C_{10}H_{16}$ hydrocarbons, and apparently no *cedrene*.

* For these details, and for specimens of sage plants and samples of German and French oils, I am indebted to the kindness of Mr. Umney, of Messrs. Wright, Layman and Umney, Southwark Street, to whom I wish to return my best thanks.

The sample with which I have now worked was a portion of that distilled in 1877, that is, two years before it was examined. This oil contained smaller quantities of $C_{10}H_{16}$ hydrocarbons than when it was last examined, but very much larger quantities both of salviol and camphor, and it also contained a considerable amount of cedrene, boiling at 260° .

It is very difficult to give any estimate of the quantities of the various constituents in any sample of sage oil, inasmuch as the oil is largely decomposed on distillation, but I should think that, roughly speaking, the latest examined sample contained about 40 per cent. of salviol, 10 per cent. of camphor, 20 per cent. $C_{10}H_{16}$ hydrocarbons, and 5 per cent. of cedrene ($C_{15}H_{24}$), the residue consisting of water and resin, non-volatile at 300° .

The sample of English-distilled oil formerly examined consisted of two portions, much the larger of which was distilled almost immediately before it was examined. The sample with which I now worked had been distilled six months before the examination was commenced.* The amount of $C_{10}H_{16}$ hydrocarbon in the former sample was about 5 per cent., in the latter about 2 per cent.; both samples consisted mainly of cedrene, but the latter (*i.e.*, the older) sample contained small quantities (perhaps 0.5 to 1 per cent.) of oil, distilling at about 200° , and having a pronounced odour of salviol. Neither sample yielded any camphor.

Now these general results undoubtedly show that the composition of sage oil varies according to the age of the sample. When first distilled the German oil is rich in hydrocarbons of the formula $C_{10}H_{16}$, contains a moderate amount of salviol, and little or no camphor; as the oil ages the amounts of salviol and of camphor increase, whilst a hydrocarbon, or hydrocarbons, of the formula $C_{15}H_{24}$ is produced. If the earliest examined sample may be regarded as a type of very old oil, then the amount of camphor in such oil is large, whilst the salviol is much reduced in quantity. I have also found that a sample of salviol prepared in the summer of 1878 contained from 2 to 4 per cent. of camphor after the expiry of 12 months. The effect of time on the composition of sage oil is therefore to increase the oxidised constituents at the expense of the $C_{10}H_{16}$ hydrocarbons, and simultaneously to produce higher isomerides of these compounds; and further, as the camphor in the oil increases in quantity the oxidised liquid constituent diminishes.

The same general results may be deduced from the examination of the two samples of English-prepared oils, but as the main constituent

* The specific gravity of English-distilled oil was given as 0.9258 at 17° ; but this oil contained a little water. I now find the specific gravity at 15° referred to water at the same temperature, to be 0.9325.

of these oils, when distilled, is a cedrene, the change of $C_{10}H_{16}$ to an oxidised compound is not so marked as in the case of the German oils.

The richness of the English oil in cedrene may be due to the fact that it was distilled wholly from the leaves of the plant.

4. Two small quantities of $C_{10}H_{16}$ hydrocarbons, boiling respectively at 156° and 167° , distilled from sage oil in 1877, and which had therefore remained in stoppered bottles containing air for two years, were submitted to fractional distillation. The greater part of each resinised; on decomposing these resins with water, separating the oil, drying, and distilling, about 20 per cent. of the 156° compound, and towards 50 per cent. of that formerly boiling at 167° , was obtained as a yellowish oil, boiling from 185° to 205° , and having a pronounced smell of salviol.

A small quantity of hydrocarbon distilled in 1876 (b. p. = 157°) was found, after three years' standing in a stoppered bottle containing air, to have resinised to a thick viscid liquid mixed with a small amount of solid matter.

This was dissolved in alcohol and the solution poured into water; a semi-solid oil separated, smelling exactly like turpentine oil, and a very small quantity of a white solid gathered at the bottom of the vessel.

These results show that the probable action of time and exposure on the $C_{10}H_{16}$ sage hydrocarbons is to produce first the liquid compound salviol, and then the solid camphor.

5. I have always found that when the *pure* hydrocarbon, $C_{10}H_{16}$, *pure* salviol (see par. 9), or *pure* cedrene is heated, no resination occurs. Further, these compounds when pure are not altered by exposure to light, whereas a mixture containing the same compounds is quickly darkened. (Sage oil itself, when kept in a colourless bottle, *very slowly* darkens in colour.)

As will be shown hereafter (par. 9), when salviol is heated, a small portion of it undergoes decomposition with production of water, and a hydrocarbon which very quickly darkens in colour and polymerises, a portion of the salviol also itself polymerising; but if the products of the very slight decomposition of the salviol be immediately removed the remainder of that compound may be boiled without change.

An investigation of the conditions of equilibrium of the chemical systems presented to us in the various essential oils would undoubtedly lead to most interesting results. Looked at generally, these conditions appear to be more in keeping with the so-called "Kinetic theory of chemical action," viz., that all systems of heterogeneous molecules tend to undergo continuous chemical changes, than with any other theory hitherto propounded.

6. In former papers it has been stated that sage oil contains two hydrocarbons of the formula $C_{10}H_{16}$, one boiling at 157° and identical with the terpene of French turpentine oil, the other boiling at or about 168° .

The 157° terpene obtained from the samples of oil examined in 1876-77 was *lævogyrate*, that separated from the German oil, soon after distillation, was *dextrogyrate*. The specific gravities and refraction equivalents of the two terpenes were practically identical.*

The results of an examination of the terpene from the present sample of German oil, *i.e.*, from oil two years after distillation, confirm those of previous papers.

There can be no doubt that sage oil contains a terpene, *i.e.*, a hydrocarbon of the formula $C_{10}H_{16}$, boiling at $156-157^{\circ}$. But does the oil contain an isomeride boiling at about 168° ?

That portion of the original distillate which came over below 190° was submitted to a prolonged fractionation over sodium, using Le Bel's apparatus. After about four weeks' continuous fractionation I was obliged to confess that the result was still doubtful. The hydrocarbons were, it seemed, oxidised by the action of sodium and air simultaneously with the reduction of the oxidised constituents of the oil; the hydrocarbons were also polymerised and resinised. I am convinced that, unless one works with very large quantities of material, long continued processes of fractionation of compounds of the terpene group, especially when mixed with oxidised derivatives such as *salviol*, are of little value. I succeeded, however, in splitting up what had formerly been regarded as a distinct hydrocarbon, boiling at 168° into a portion consisting of terpene, and another portion boiling at about 171° , but whether this would not itself be further decomposed if it were fractionated in quantity I cannot pretend to determine.

The supposed hydrocarbon boiling at 168° examined in 1876-77 (*Phil. Mag., loc. cit.*) undoubtedly contained *salviol* (see *sp. gr.*, action of heat, refraction equivalent, and odour).

That described in 1878 in this Journal was probably much purer, but it may have been a mixture. It has been already stated that pure English-distilled oil yielded about 5 per cent. of a hydrocarbon boiling at $166-171^{\circ}$; the second sample obtained from the same source yielded about 2 per cent. boiling at about 170° .

These two liquids were mixed and again fractionated, and about 5 c.c. of a colourless oil boiling from $170-171^{\circ}$ was obtained. From the physical data determined for this liquid (see Appendix, p. 690), and

* The figure given as the specific gravity of the terpene in the paper by Sigiura and Muir (this Journal, 1878; *Proc.*, p. 292), is a *lapsus pennæ*; it should have been 0.8635, not 0.8435.

from those determined for the similar liquid obtained from the German oil, it seems probable that sage oil does contain an isomeride of terpene, boiling somewhere about 170° — 175° .

This liquid, as also the terpene boiling at 156° , gave the reactions for dihydrochloride by Ribau's test. The comparative difficulty with which the dibromide, obtained by adding bromine to the liquid boiling at about 170° , is decomposed on distillation (*Phil. Mag., loc. cit.*), as also the production of oxalic acid by oxidising this liquid with dilute nitric acid, tend, on the whole, to confirm the supposition that sage oil contains an isomeride of terpene. The fractionation of large quantities of oil boiling at about 170° can, however, alone determine the existence or non-existence of the supposed hydrocarbon. Until certain of the actual existence of such a compound I forbear to add *salvene* to the already too long list of isomerides of terpene.

7. I now proceed to detail the results of the examination of the individual constituents of sage oil. The chemical work done was almost entirely confined to experiments with salviol and sage camphor.

The action of phosphoric anhydride, phosphorus pentachloride, and of bromine on salviol, has been examined; but as the quantities of material at my disposal were comparatively small, I shall give only the general results of the action, omitting all details of fractionation, &c.

Salviol, when heated with an excess of phosphoric anhydride for a considerable time, was resinised, with the exception of about one-fourth of the quantity originally used. The non-resinised portion consisted chiefly of a $C_{10}H_{16}$ hydrocarbon, boiling at about 172° , and probably identical with the hydrocarbon of this formula, and boiling about this point, which experiments indicate to be existent in sage oil. A small quantity of a paraffin-like hydrocarbon, which was unacted on by strong sulphuric acid, was also produced; this was probably identical with the $C_{10}H_{20}$ hydrocarbon obtained by Armstrong and Tilden by the action of sulphuric acid on French and American turpentine (this Journal, 1879; *Trans.*, p. 733), and by the former of these chemists by the action of iodine on camphor (*Ber.*, 11, 151). The lower boiling fractions contained a very small quantity of a hydrocarbon, which was shown by its qualitative reactions to be, almost certainly, a benzene.

The resinous product of the action was unacted on by sodium, and appeared to be free, or nearly free, from polymerides of salviol, but to consist mainly of polymerides of $C_{10}H_{16}$; it was almost unacted on by concentrated sulphuric acid, and was non-volatile in steam. No cymene was found in the product of the action of phosphoric anhydride on salviol.

These results almost oblige us to regard salviol as $C_{10}H_{16}O$, and not as $C_{10}H_{16}O$, as formerly supposed.

Phosphorus pentachloride exerted no action on salviol at ordinary

temperatures. On heating the two substances together hydrochloric acid was evolved, and a dark-coloured oil was obtained, which could not be distilled without decomposition. On repeated distillation over sodium this oil yielded a $C_{10}H_{16}$ hydrocarbon, boiling at a temperature higher than 157° , and a small quantity of a hydrocarbon, other than cymene, boiling about 170° , and unacted on by concentrated sulphuric acid.

Bromine acted on salviol with evolution of much hydrobromic acid and production of considerable quantities of a yellow-red oil, which was decomposed on distillation with separation of carbon. It has been before shown (Sigiura and Muir, *loc. cit.*) that under certain conditions a brominated derivative of salviol is obtained, which on exposure to air slowly deposits crystals of camphor. From the reaction of the brominated oil now obtained it is very probably an addition-product, and the production of camphor from this oil may be represented as $C_{10}H_{16}Br_2O = C_{10}H_{16}O + 2HBr$.

8. The production of camphor melting at 174° by oxidising salviol with chromic liquor has been fully confirmed. The ready oxidation of salviol to camphor explains the fact that the amount of camphor in sage oil increases as the oil ages.

I was for some time inclined to believe that camphor was produced during the fractionation of those portions of the oil boiling about 200° , but careful experiments with oil from which no camphor separated at -15° , have shown that this is not the case. That the prolonged action of air and diffused sunlight on salviol, even at ordinary temperatures, does, however, convert a portion of it into camphor is evidenced by the fact that salviol, which in the summer of 1878 was free from camphor, contained about 3 per cent. of this substance in the summer of 1879.

The production of an oil (noticed in a former paper) by treating salviol with nitric acid, which on decomposition with water yielded camphor, is evidently to be traced to the secondary action of the acid on the camphor produced; inasmuch as I find that sage camphor is dissolved by 1 : 1 nitric acid, and that addition of water to the yellow oil so formed causes a reprecipitation of camphor.*

9. When perfectly dehydrated salviol was boiled it suffered very slight decomposition with production of a little water and slight darkening in colour, but by far the greater portion distilled unchanged. The slightly darkened oil was shown to contain traces of polymerised substances, probably polymerides of salviol and of $C_{10}H_{16}$ hydrocarbons; not a trace of cymene was found.

This reaction, as well as the production of camphor by oxidising salviol, points to the formula $C_{10}H_{18}O$.

* This reaction may be advantageously applied to the purification of sage camphor.

10. In a former paper (*Phil. Mag., loc. cit.*) the results of two combustions of salviol were detailed, giving respectively, *hydrogen*, 10·31 and 10·67; *carbon*, 78·83 and 78·86 per cent.

Mr. Alfred J. King, of the Owens College, has been so good as to make several combustions of salviol apparently free from camphor, and boiling at 200—201°; his results are annexed:—

	Gram H ₂ O.	Gram CO ₂ .
1. 0·2685 gram gave	0·2620	—
2. 0·1665 „ „	0·1686	0·4785
3. 0·3035 „ „	0·2905	0·8735
4. 0·3030 „ „	0·2895	0·8730
5. 0·2570 „ „	0·2515	0·7390

	Calculated for			Found.					
	C ₁₀ H ₁₆ O.	C ₁₀ H ₁₈ O.	I.	II.	III.	IV.	V.	Mean.	
Carbon ..	78·94	77·92	—	78·37	78·49	78·58	78·42	78·46	
Hydrogen	10·52	11·68	10·84	11·24	10·63	10·62	10·87	10·84	

Difference of mean from

	C ₁₀ H ₁₆ O.	C ₁₀ H ₁₈ O.
Carbon	—0·48	+0·54
Hydrogen	+0·32	—0·84

If these numbers be compared with those formerly obtained, the carbon is found to be now 0·38 lower, and the hydrogen 0·34 higher than then.

Regarding the reactions of salviol already described, I think that the conclusion appears inevitable that this compound should be formulated C₁₀H₁₈O. The discrepancies between the above numbers and those calculated from this formula are most probably due to the retention by the salviol of small quantities of camphor.

11. Camphor separates from sage oil chiefly from the fraction boiling between 205° and 208°; it is partially soluble in salviol, but separates almost completely therefrom at —15°.

The melting point of sage camphor, after eight sublimations, was found to be 174°, and the boiling point 205° (both uncorr.), *i.e.*, the same as those of laurel camphor.

Phosphorus pentachloride readily acted on sage camphor with production of an oil, which was decomposed by water, yielding a wax-like solid, melting at about 80°, and decomposed by heating with sodium with formation of a white solid different in smell and melting point from the original solid (see *Montgolfier*, “Action of Sodium on C₁₀H₁₆Cl₂ and C₁₀H₁₆Cl,” *Ann. Chim. Phys.*, **14**, 5).

12. When sage camphor was oxidised by long-continued boiling

with 2 : 1 nitric acid it yielded optically inactive camphoric acid, melting at 186°.

13. Carbonic anhydride was found to react on sage camphor, dissolved in toluene, in presence of sodium with production of a solid melting at 199—200°, possessing the properties of camphol, and being optically inactive: the liquid separated from this camphol when neutralised with hydrochloric acid yielded a small quantity of a nearly colourless solid, melting at above 100°, slightly soluble in water, and giving in aqueous solution a white precipitate with lead acetate, therefore most probably consisting of camphocarbonic acid.

The melting and boiling points of sage camphor, the action of nitric acid, of phosphorus pentachloride and pentasulphide (formerly shown to result in production of cymene), and the action of carbonic anhydride in presence of sodium, all point to the inference that this camphor is "chemically identical" with laurel camphor. The optical behaviour of solutions of these compounds is different; but this is probably connected more with the grouping of molecules than with the structure of the molecules themselves.

14. It has been already stated that the samples of oil distilled from the leaves of the common English sage all contained as main constituent a hydrocarbon of the formula $C_{15}H_{24}$, isomeric or identical with cedrene from cedar oil (Gladstone, this Journal [2], 10, 1).

The boiling point of sage cedrene after repeated distillation is about 260° (in a former paper it was given as 264—271°, but this is certainly too high).

The colour of the cedrene from the second sample of English-distilled oil was of a yellower shade of green than that from the earlier sample, the value obtained for the refractive index for mean rays of each oil was, however, the same; the boiling points were also identical.

The cedrene from the last sample of German oil with which I have worked was of dark emerald-green colour, resembling that of the same hydrocarbon from the earlier sample of English oil. The specific gravity, &c., are detailed in the Appendix.

Sage cedrene is almost certainly optically inactive (this Journal, 1878, *Proc.*, p. 298). Sulphuric acid (4 : 1) resinised sage cedrene, even when surrounded by a freezing mixture. About one-fourth of the total quantity was obtained seemingly unchanged by steam distillation.

Hydrochloric acid gas acted on sage cedrene dissolved in ether with production of a purple-coloured oil, which was slowly decomposed on distillation in steam with reproduction of about 25 per cent. of the original cedrene, and a considerable quantity of resin.

Summary.

1. The composition of essential oil of sage varies with the age of the oil. Soon after distillation the oil contains comparatively small quantities of salviol, camphor, and cedrene; the quantities of these—especially of the two former—increase as the oil ages. Probably salviol is first produced by oxidation of the $C_{10}H_{16}$ compound present, and camphor is the product of the further oxidation of salviol.

Oil of sage distilled from the leaves of the English plant is characterised by the presence of much cedrene, boiling at about 260° , with very little $C_{10}H_{16}$ hydrocarbons, and only traces of oxidised compounds.

2. The terpene of sage oil is almost certainly identical with that from French turpentine. The existence in sage oil of an isomeride of terpene, boiling at about 171° , is probable, but cannot yet be regarded as finally determined.

3. Salviol has the formula $C_{10}H_{16}O$, and not $C_{10}H_{18}O$, as formerly supposed; on oxidation with chromic liquor or dilute nitric acid, it yields camphor, melting at 174° , as also oxalic and acetic acids.

4. Salviol is very slightly decomposed on distillation, with production of water, and a $C_{10}H_{16}$ compound or compounds, which is at the same time very slightly polymerised.

The prolonged action of sunlight in presence of air on the $C_{10}H_{16}$ compounds of sage oil probably results in the production of salviol, and if the time be very long, of small quantities of camphor. The prolonged action of light on salviol certainly causes the formation of camphor.

5. The action of phosphoric anhydride on salviol is very complex; the main resultants appear to be polymerides of $C_{10}H_{16}$, a hydrocarbon of this formula boiling at about 171° , a hydrocarbon of the benzene series boiling below 130° , and a paraffin-like hydrocarbon boiling between 170° and 180° . Cymene is not found among the products of this action, when the action is continued for some time.

6. The actions of phosphorus pentachloride, and of bromine on salviol, have not been fully studied. The former, which takes place only at temperatures above the ordinary, results in the production of a chlorinated derivative, which is decomposed on distillation, with formation of a $C_{10}H_{16}$ hydrocarbon, boiling above 157° , and probably accompanied by the same paraffin-like compound, which is one of the products of the action of phosphoric anhydride on salviol.

Salviol is very energetically attacked by bromine, with elimination of much hydrogen, and setting free of carbon; a brominated oil may, however, be separated, and, under special conditions, small quantities of camphor, melting at 174° , are produced.

7. Camphor separates chiefly from those portions of sage oil which

distil from 205—208°. This camphor is partially soluble in salviol, but, if the solution be concentrated, separates therefrom at about —15°. Sage camphor melts at 174°, and boils at 205° (uncorr.). In its reactions with phosphorus pentachloride and nitric acid, and in the fact that camphoric acid, melting at 186°, is obtained by its oxidation, sage camphor appears to be chemically identical with laurel camphor. Sage camphor, as also the camphoric acid obtained from it, is, however, optically inactive.

Sage camphor yields a camphol, melting at 199—200° (and most probably a camphocarbonic acid), when submitted to the action of carbonic anhydride in presence of sodium. The camphol thus obtained is optically inactive.

8. Sage cedrene, boiling about 260°, has been only very partially examined. About 80 per cent. is resinised (polymerised?) by 4 : 1 sulphuric acid, whilst hydrochloric acid appears to form a hydrochloride, which is almost entirely decomposed by steam distillation, with the re-formation of about 25 per cent. of the original cedrene.

9. The compounds present in sage oil are fairly stable when pure, but when mixed even with small quantities of other bodies, they undergo cycles of chemical change. Processes of oxidation, deoxidation, and polymerisation, most probably occur simultaneously during the ageing, and also during the fractionation of sage oil.

APPENDIX TO PAPER "ON ESSENTIAL OIL OF SAGE."

By M. M. PATTISON MUIR.

Some Optical Properties of Constituents of Sage Oil.

My best thanks are due to my friend, Mr. R. E. Day, M.A., of King's College, London, for his great kindness in making many measurements of the refractive indices of the constituents of sage oil.

The constituents of sage oil, separated as described in the preceding paper, cannot be regarded as pure; for this reason, and also because of the small quantities at my disposal, I have contented myself with determining only a few of the physical properties of these compounds; nor (while conducting these determinations with care) have I sought to carry out the measurements with extreme refinement.

In volume 12 of the *Berichte*, a paper appeared by Brühl (p. 2135), in which a formula is given for finding the true refraction coefficient (A) of a substance from determinations of the refractive indices for

two rays. By substituting A for μ in the ordinary formula, $\frac{\mu-1}{d}$, a constant is obtained for each substance, the value of which is independent of dispersion and temperature, and dependent only on the chemical structure of the substance examined. By multiplying this constant by the molecular weight of the substance, the *molecular refraction* is obtained.

The formulæ used for obtaining the value of A are as follows:—

$$\begin{aligned} \mu\lambda_1 &= A + \frac{B}{\lambda_1^2} & \text{Hence } B &= \frac{\mu\lambda_2 - \mu\lambda_1}{\frac{1}{\lambda_2^2} - \frac{1}{\lambda_1^2}} \\ \mu\lambda_2 &= A + \frac{B}{\lambda_2^2} & \text{and } A &= \mu\lambda_1 - \frac{B}{\lambda_1^2} \end{aligned}$$

where $\mu\lambda_1$ is the observed index for light of wave-length λ_1 , and $\mu\lambda_2$ the observed index for light of wave-length λ_2 .

In the following determinations the refractive indices were measured for the red hydrogen line, $H\alpha$, and for the violet line, $H\gamma$. Taking the wave-lengths of these lines as 3968 and 3933 respectively, we get $\frac{1}{\lambda_2^2} - \frac{1}{\lambda_1^2} = 0.000\,000\,03$.

In calculating the molecular refractions of the compounds examined, I have used Brühl's numbers for the atomic refraction of carbon, hydrogen, and oxygen, viz., $C = 4.86$, $H = 1.29$, and $O = 2.90$.

Specific gravities are referred to water at the same temperature as that at which the determinations were made.

Sage Terpene, *b. p.* = 157° . *Separated from German Oil.* (*Dextro-rotatory.*)—The data obtained were as follows. (Temp. = 15°):—

$$\mu H\alpha(\mu\lambda_1) = 1.4649. \quad \mu H\gamma(\mu\lambda_2) = 1.4755.$$

Sp. gr. at $15^\circ = 0.8635$.

Hence $\frac{A-1}{d} \cdot M = 72.7$; calculated = 69.3; difference = 3.4,

which is nearly equal to the mean difference obtained by Brühl for that class of carbon compounds containing two pairs of "doubly-linked" carbon atoms.

$C_{10}H_{16}$ *Hydrocarbon, boiling at about 170° . Separated from German Oil.* (*Dextro-rotatory.*)—Temp. = 15° .

$$\mu H\alpha = 1.4635. \quad \mu H\gamma = 1.4755. \quad \text{Mean value of } \mu = 1.4695.$$

Sp. gr. at $15^\circ = 0.8653$.

Taking the mean value of μ we get $\frac{\mu-1}{d} \cdot M = 73.8$.

$C_{10}H_{16}$ *Hydrocarbon, boiling about 170° . Separated from English Oil.*

(*slightly lævorotatory*.)—Mean value of $\mu = 1.4698$ (15°). Sp. gr. at $15^\circ = 0.8667$. Hence $\frac{\mu - 1}{d} \cdot M = 73.7$.

As I cannot be certain of the purity of this hydrocarbon (see paper on "Sage Oil," par. 6), I have not applied Brühl's formula. The value of $\frac{\mu - 1}{d} \cdot M$ is constant, whether the data be those obtained for the hydrocarbon from German, or for that from English oil; the difference between this and the calculated value is about equal to the difference observed in the case of sage terpene.

Terpene distilled in 1876, and redistilled in 1879 (see paper, par. 4). (15° .)

$\mu_{H\alpha} = 1.4658$. $\mu_{H\gamma} = 1.4796$. Mean value of $\mu = 1.4727$.

Taking the former sp. gr. (0.8635), we have $\frac{\mu - 1}{d} \cdot M = 74.3$ which is nearly the same as the value obtained for the freshly distilled terpene. This terpene was lævorotatory; it was also lævorotatory in 1876.

Salviol, b.p. = 200° . Separated from German Oil. (Dextrorotatory.) (15° .)

$\mu_{H\alpha} = 1.4559$. $\mu_{H\gamma} = 1.4733$. Sp. gr. at $15^\circ = 0.938$.

Hence $\frac{A - 1}{d} \cdot M = 74.2$; calculated = 74.7 . Hence by Brühl's rule salviol contains no "doubly linked" pairs of carbon-atoms.

Cedrene boiling about 260° . Separated from German oil. (Inactive.) (15° .)

$\mu_{H\alpha} = 1.4996$. $\mu_{H\lambda} = 1.5147$. Mean value of $\mu = 1.5071$.

Cedrene separated from first sample of English oil. Mean value of μ at $15^\circ = 1.4979$. The same number was obtained for the cedrene separated from the second sample of English oil. Hence mean value of μ for all cedrenes = 1.5025 . Mean sp. gr. at $15^\circ = 0.915$.* As none of the cedrenes are quite free from other liquids, I have simply calculated the value of $\frac{\mu - 1}{d} \cdot M$, and find it to be = 111.9 ; calculated = 103.9 ; difference = 8.0 ; which by Brühl's rule shows four pairs of "doubly linked" carbon-atoms in sage cedrene.

If there be in sage oil an isomeride of terpene, boiling at about 170° , these results show that it probably belongs to the same type of $C_{10}H_{16}$

* From the data given in a former paper (Sigiura and Muir, this Journal [1], 1878, 278), the value of d at 15° for cedrene from English oil is found to be = 0.912 . The value of d as directly determined for the cedrene from German oil was = 0.918 (15°). Hence the mean specific gravity of sage cedrene at 15° is = 0.915 .

hydrocarbons as terpene itself, *i.e.*, to the type containing two pairs of "doubly linked" carbon-atoms; whilst on the other hand salviol appears to have all its carbon atoms "singly linked." If the formulæ given by Armstrong for terpene and camphor (*Ber.*, 12, 1698) be adopted,* we should have the $C_{10}H_{16}$ hydrocarbon of sage classed with those of citron oil, orange oil, &c., whilst salviol must be closely allied to camphor. The passage from this hydrocarbon to salviol appears to be attended with a loosening of the double links of the two pairs of carbon-atoms; but at the same time the polymerisation of the $C_{10}H_{16}$ to $C_{15}H_{24}$ is accompanied by a further process of "double linking." In the paper on sage oil reasons have been given in favour of regarding the oxidation, hydration, and polymerisation of $C_{10}H_{16}$ hydrocarbons as simultaneously occurring changes.

I have sought to apply Brühl's formula to the data obtained by other observers for a few oxidised oils, and for cedrene (see especially Gladstone, this Journal [2], 10, 1; and this Journal, 11, 972); but the results (a few of which are annexed) seem to indicate that these oils have not been free from impurities when their refractive indices were determined.

Difference between observed and
calculated values for

$$\left(\frac{A-1}{d}\right) \cdot M.$$

Citronellol, $C_{10}H_{18}O$	4·8
Cajeputol, $C_{10}H_{18}O$	1·5
Myristicol, $C_{10}H_{16}O$	3·4
Absinthol, $C_{10}H_{16}O$	3·3

In the hydrocarbons of the formula $C_{15}H_{24}$, the value of the difference varies from 4·4 to 7·0.

LXIII.—On the Synthetical Production of New Acids of the Pyruvic Series.

By L. CLAISEN, Ph.D., and E. MORITZ.

PART I. Propionylformic Acid.

DR. CLAISEN showed some time ago that the cyanides of the acid radicles could, under favourable circumstances, be converted into corresponding acids in the same way as the cyanides of alcohol-radicles, benzoyl cyanide being the one used for experiment.

* The results of this paper give a general confirmation to these or similar formulæ.

Later on, Claisen (*Ber.*, **10**, 429, 844, 1663) and Shadwell (*Ber.*, **13**, 6) proved that acetyl cyanide reacts in the same way. We therefore thought that it would be interesting to follow up this reaction with homologous fatty acid cyanides, *e.g.*, to produce propionylformic acid from propionyl cyanide.

These reactions are interesting theoretically, as other ketonic acids exist which are partly stable and partly unstable. Take for example the three normal ketonic acids of the formula $C_3H_5O_3$:—

Acetopropionic acid.	$COOH.CH_2.CH_2(CO.CH_3)$ stable.
Propionylacetic acid.	$COOH.CH_2(CO.CH_2CH_3)$ unstable.
Butyrylformic acid	$COOH(CO.CH_2.CH_2CH_3)$ stable.

The general method employed was that of Claisen and Shadwell, substituting propionyl chloride for the acetyl chloride used by them.

The great difficulty we found was to get a better method for making the acid cyanide; and in spite of numerous experiments, we had to fall back upon Hübner's (*Annalen*, **120**, 334) method, which consists in heating the acid chloride (in this case propionyl chloride) with silver cyanide in closed tubes for an hour at 100° . We found that 12 grams of propionyl chloride and 8 grams of silver cyanide gave the best yield. The contents of all the tubes used was then transferred to a large flask, and the whole was distilled off over a sand-bath into a fractioning flask. The liquid was then accurately fractionated. The propionyl cyanide came over between 100 — 115° . This, when repeatedly fractionated, gave the pure cyanide, which boiled at 108 — 109° . The following are results obtained by analysis :—

	Theory.		Found.	
C ₄ ..	48	57.83	58.27	0.2401 gram substance gave $\left\{ \begin{array}{l} 0.513 \text{ CO}_2 \\ 0.1289 \text{ H}_2\text{O} \end{array} \right.$
H ₅ ..	5	6.02	5.96	
N ₁ ..	14	16.87	16.76	
O ₃ ..	16	19.28	—	$\left\{ \begin{array}{l} 0.3198 \text{ gram substance gave } 0.513 \text{ gram} \\ \text{AgCN, corresponding to } 0.0536 \text{ nitrogen} \end{array} \right.$
	83	100.00		

The nitrogen was determined in the form of silver cyanide. On sealing up propionyl cyanide with a few drops of nitric acid, silver nitrate and water, the silver cyanide is precipitated quantitatively.

On fractionating the residue, a polymeric cyanide distils over at a temperature of about 100° higher than the cyanide: of this we shall speak hereafter.

Propionylformic Amide, $CH_3.CH_2.CO.CONH_2$.

To prepare this compound, a number of small test-tubes provided with well-fitting corks were each charged with 2 grams of the cyanide

and 1 gram of hydrochloric acid of sp. gr. 1.23. This is approximately one molecular proportion of cyanide to one of water contained in the acid. The test-tubes were then left for two hours in iced water. By that time the liquids were thoroughly mixed, and hydrochloric acid gas was given off violently, very often blowing the cork out. The mass then became semi-solid, and was placed on to seven or eight watch-glasses, and these were left over lime for several days. The mass, consisting of crystallised soda amide and ammonium chloride, was fractionally sublimed, the amide subliming at a much lower temperature than ammonium chloride. When pure it fuses at 116—117°.

When analysed it gave the following results :—

- (1.) 0.1003 gram substance gave 0.174 CO₂ and 0.065 H₂O.
- (2.) 0.1052 " 0.183 CO₂ and 0.069 H₂O.
- (3.) 0.1505 " 0.2629 CO₂ and 0.097 H₂O.
- (4.) 0.151 " 0.1433 Pt.

			Found.		
			I.	II.	III.
C ₄	48	Theory. 77.53	47.31	47.44	47.64
H ₇	7	6.93	7.20	7.28	7.16
N.....	14	13.86	13.46	—	—
O ₂	32	31.68	—	—	—

101

Instead of preparing our acid from the amide as Claisen and Shadwell did, we produced it directly from the cyanide, thereby getting a much larger yield. 36 grams of cyanide were brought together with hydrochloric acid of sp. gr. 1.23, in portions of 5 grams of cyanide to 2.5 of acid (approximately one molecular proportion of cyanide to one of water), and the mixture was left to stand for two hours in iced water till the conversion was complete. To each portion was then added 2.5 grams more hydrochloric acid of the same specific gravity, so that each molecular proportion of cyanide was brought into contact with two of water. After standing for a little while the semi-solid mass was transferred into a flask provided with an inverted condenser, and so much hydrochloric acid of sp. gr. 1.1 added as to convert all the ammonia into ammonium chloride. The vessels were then rinsed out with a little distilled water, and the water added to the rest. The whole mixture was then boiled for two or three hours on the water-bath. On cooling, ammonium chloride separated out.

At the end of three hours enough water was added to dissolve the ammonium chloride, and the liquid was then shaken up for some time

with small portions of ether. The ethereal solution was then dried over calcium chloride and the ether boiled off. The residue consisted of propionylformic acid and a little propionic acid. Propionic acid boils at 57° under a pressure of 25 mm., whereas propionylformic acid boiled at $70-80^{\circ}$. When pure, its boiling point at the same pressure is $74-78^{\circ}$. Between $70-80^{\circ}$ we obtained 18° of our acid.

Propionylformic acid is an oily liquid, having a characteristic burnt smell; its sp. gr. is 1.12. It does not solidify at -15° .

When analysed it gave the following results:—

- (1.) 0.313 gram substance gave 0.5382 CO_2 and 0.178 H_2O .
 (2.) 0.3595 ,, 0.6191 CO_2 and 0.2004 H_2O .

			Found.	
			I.	II.
C ₄	48	Theory. 47.06	46.89	46.96
H ₆	6	5.88	6.31	6.19
O ₃	48	47.06	—	—
		100.00		

The theoretical values for propionic acid are, $\text{C } 48.64$, $\text{H } 8.11$, from which it can be seen that we obtained our acid in a very pure condition.

It dissolves in water, alcohol, and ether, in all proportions. When diluted and treated warm with silver carbonate, it gives a beautifully crystalline silver salt, $\text{CH}_3\text{CH}_2\text{CO.COOAg}$, which is moderately soluble in cold water. The prismatic crystals always form at right angles to one another.

The following are two silver determinations:—

- (1.) 0.1961 gram substance gave 0.1014 Ag.
 (2.) 0.2083 ,, 0.1077 Ag.

			Found.	
			I.	II.
C ₄	} 101	Theory. 48.33	—	—
H ₅				
O ₃				
Ag	108	51.67	51.70	51.70
		209	100.00	

An aqueous solution of the acid when treated with barium carbonate gives a characteristic barium salt of the form $(\text{C}_4\text{H}_5\text{O}_3)_2\text{Ba} + \text{OH}_2$. Between $160-170^{\circ}$ it decomposes.

The following analyses prove its constitution:—

0.001

Dried at 100°.		Theory.	Found.	
			I.	II.
$[\text{C}_4\text{H}_5\text{O}_3]_2$	202	59·59	—	—
Ba.....	137	40·41	40·42	40·48
	339	100·00		

Water estimation.		Theory.	Found.
$[\text{C}_4\text{H}_5\text{O}_3]_2\text{Ba}$	339	94·96	—
OH_2	18	5·04	4·77
	357	100·00	

This salt is of the same form as the corresponding barium propionate, but the latter contains 48·41 of barium, and is very soluble in water, whereas barium propionylformate is only moderately soluble.

By treating the calcium salt with mercurous nitrate, a crystalline mercurous propionylformate is formed, which, however, is extremely unstable.

Propionylformic acid does not give an insoluble basic salt when treated with barium hydrate. This reaction affords less characteristic distinction between the behaviour of propionylformic acid and pyruvic acid under the same circumstances.

Reduction of Propionylformic Acid.

Just as pyruvic acid is converted by hydrogen into acetic acid, so may propionylformic acid be reduced by the action of nascent hydrogen to normal and hydroxybutyric acid. Perfectly pure crystals of this acid were obtained melting at 42—43°.

On the whole the acid is very stable, thereby differing greatly from its isomeride *aceto-acetic acid*, which can exist only in the form of an ether.

Note on the Polymeride Dipropionyl Dicyanide.

If in the distillation of propionyl cyanide, the residue be subjected to accurate fractional distillation, an oily liquid comes over between 200—210°. When perfectly pure it boils at 208°. Curiously enough it cannot be solidified at -15°, although its homologue diacetyl dicyanide is a crystalline solid at the ordinary temperature. We had so little that we could not study its reactions.

The following were the analytical results:—

0·1844 gram substance gave 0·3925 CO_2 .

0·1054 H_2O .

0·2492 gram substance gave 0·292 Pt.

		Theory.	Found.
C ₄	48	57·83	58·05
H ₅	5	6·02	6·35
N.....	14	16·87	16·62
O.....	16	19·28	—
	93	100·00	

The vapour-density cannot be determined according to Victor Meyer's method, as the substance decomposes when heated to the temperature required. Hofmann's method had to be used; the mean of many determinations gave a result which left no doubt as to the compound in question being the double cyanide.

In our next paper we hope to be able to publish some interesting reactions of these polymeric cyanides, as we have since obtained them in much larger quantities.

LXIV.—CONTRIBUTIONS FROM THE LABORATORY OF THE ROYAL COLLEGE OF CHEMISTRY.

On the Action of Nitric Acid on Diparatolylguanidine.

By A. G. PERKIN.

THIS investigation was originally undertaken with a view to the study of diparatolylguanidine and its cyanogen derivatives; but having subsequently learnt that Herr Oscar Landgrebe in his paper "On the Cyanogen Derivatives of Guanidine" (*Ber.*, 10, 1587) had already worked on the subject, it appeared more desirable to confine my attention to the investigation of one or two reactions which were noticed whilst experimenting with this base. The first selected was its behaviour with nitric acid.

Preparation of Diparatolylguanidine.

This base was first prepared by W. Wilson (*Chem. Soc. Qu. J.*, 3, 154) by the action of chloride of cyanogen on toluidine (evidently the "para" body); since then Dr. A. W. Hofmann obtained it by the action of ammonia and lead oxide upon ditolylthiocarbamide. For the purposes of this investigation, however, I used the former process, which works very satisfactorily. In the purification of the crude base, I found the use of petroleum spirit to remove any unaltered toluidine very effective. The diparatolylguanidine was obtained in

beautiful white transparent needles, which gave on analysis the following numbers :—

·2449 gram of substance gave—

·6412 „ „ CO₂, and

·1576 „ „ OH₂.

	Theory for C ₁₅ H ₁₇ N ₃ .	Experiment.
Carbon	75·31	75·46
Hydrogen	7·11	7·19

Action of Nitric Acid on Diparatolyguanidine.

Nitric acid (sp. gr. 1·5) acts energetically on this base, dissolving it with evolution of heat and formation of red fumes. To moderate this action, the powdered base was added to the fuming acid in small quantities at short intervals, any considerable rise of temperature being avoided. On adding the brown-red solution thus obtained to a large excess of water, a certain amount of product was precipitated, consisting chiefly of resinous matter,* which was filtered off and well washed to remove soluble compounds. Ammonia in excess was then added to the clear filtrate. This caused the separation of a chrome-yellow precipitate, which was washed and dissolved in water acidulated with hydrochloric acid. After filtration, dilute nitric acid was added, when a crystalline nitrate rapidly separated. After standing for about 24 hours, this salt was collected, slightly washed, pressed between bibulous paper, and purified by one or two crystallisations from alcohol. It was then dissolved in water, and the base thrown down with ammonia. This was then washed, dried, and crystallised from alcohol. On analysis, it gave the following numbers :—

I. ·11975 gram of substance gave—

·2380 „ „ CO₂, and

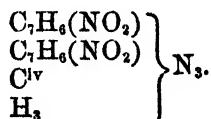
·0482 „ „ OH₂.

II. ·1053 „ „ substance gave—

·2109 „ „ CO₂, and

·0396 „ „ OH₂.

These numbers give percentages closely agreeing with those required by the formula C₁₅H₁₅N₃O₄ or dinitrodiparatolyguanidine; thus :—



* This resinous body when purified crystallises from alcohol in brilliant yellow needles, but has not been further investigated.

	Theory.	Experiment.	
		I.	II.
Carbon	54.71	54.28	54.62
Hydrogen.....	4.54	4.47	4.18

Dinitrodiparatolylguanidine melts with decomposition at about 197°. It is difficultly soluble in cold, but moderately in boiling alcohol. It crystallises from this solvent in small beautiful orange-red prisms. It is insoluble in water. Its alcoholic solution, when treated with tin and hydrochloric acid, gives a product crystallising in needles, which is probably an amido-derivative. It is under investigation.

The *nitrate*, the preparation of which has already been given, crystallises from alcohol, in which it is only moderately soluble, in small flat needles of a pale straw colour. On analysis, it gave the following numbers:—

- I. .12585 gram of substance gave—
 .2112 „ „ CO₂, and
 .0467 „ „ OH₂.
 II. .1529 „ „ substance gave—
 .275 c.c. of N at 757.5 mm. and 16°C.

These numbers give percentages agreeing with the formula
 C₁₅H₁₅N₅O₄.HNO₃.

	Theory.	Experiment.	
		I.	II.
Carbon	45.95	45.84	—
Hydrogen.....	4.08	4.12	—
Nitrogen	21.42	—	20.98

The aqueous mother-liquors from the preparation of this nitrate from diparatolylguanidine contain another base crystallising in yellow needles. This, however, has not yet been obtained in a perfectly pure state. Its fusing point is considerably higher than that of the base just described, and as it contains less carbon and hydrogen, it is not improbably a *trinitro*-compound.

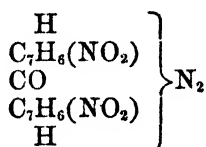
Action of Nitric Acid in presence of Alcohol on Diparatolylguanidine.

If a quantity of diparatolylguanidine be suspended in alcohol, as much nitric acid (sp. gr. 1.4) added as alcohol, and the mixture heated, violent chemical action soon takes place between the acid and alcohol; but after a short time a second reaction sets in, attended with very copious evolution of red fumes, and at the same time with the formation of a crystalline yellow body. To purify this, water was

added, the mixture thrown on a filter,* and the insoluble product washed first with water and then with alcohol. It was then crystallised from alcohol and afterwards from coal-tar naphtha, from which it was deposited in fine needles, usually of a pale primrose, but sometimes of an orange colour. This difference in colour was apparently due to a physical, and not to a chemical difference, as was determined by analysis (see Analysis III). Moreover, when it was recrystallised, the orange colour not unfrequently changed suddenly to a primrose without any apparent separation of impurities. On analysis, this substance gave the following numbers:—

I.	·1331	gram of substance gave—
	·2668	„ „ CO ₂ , and
	·0520	„ „ OH ₂ .
II.	·0964	„ „ substance gave—
	·1918	„ „ CO ₂ , and
	·0352	„ „ OH ₂ .
III.	·1002	„ „ substance gave—
	·2104	„ „ CO ₂ , and
	·0395	„ „ OH ₂ .
IV.	·2108	„ „ substance gave—
	30·4	c.c. N at 769 mm. and 11° C.
V.	·2024	gram of substance gave—
	29·25	c.c. N. at 769 mm. and 12° C.

These numbers give percentages agreeing with those required by the formula $C_{13}H_{14}N_4O_6$, representing *dinitroparatolylurea*, which may be written thus:—



	Theory.	Experiment.				
		I.	II.	III.	IV.	V.
Carbon	54·54	54·66	54·25	54·81	—	—
Hydrogen ..	4·24	4·34	4·05	4·38	—	—
Nitrogen....	16·97	—	—	—	17·38	17·27

Dinitrodiparatolylurea melts with decomposition at about 233°. It is rather difficultly soluble in boiling alcohol, but more freely in boiling coal-tar naphtha.

* The aqueous washings were found to contain a small quantity of the nitrate of dinitrodiparatolylguanidine.

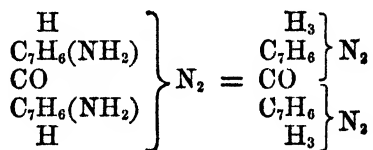
Reduction of Dinitroparatolyurea.

On boiling this urea in alcohol with hydrochloric acid and granulated tin, it gradually dissolves and eventually forms a colourless solution. From this the alcohol was removed by boiling with water, and the tin by means of sulphuretted hydrogen. The solution thus obtained was found to contain the hydrochloride of a new base. To obtain the base, the solution was evaporated to dryness over a water-bath and the hydrochloride dissolved in boiling alcohol. Ammonia was then added, which caused the base to crystallise out rapidly in fine needles. These were collected, washed with alcohol, then with water, and afterwards dried.

On analysis this substance gave the following numbers:—

- I. .0891 gram of substance gave—
 .2168 „ „ CO₂, and
 .0565 „ „ OH₂.
 II. .1054 „ „ substance gave—
 18.37 c.c. N at 751.5 mm. and 15° C.

These numbers gave percentages agreeing with those required by the formula, C₁₅H₁₈N₄O, which represents *diamidoparatolyurea*, or the carbamide of paratolylenediamine, thus:—



	Theory.	Experiment.	
		I.	II.
Carbon	66.66	66.36	—
Hydrogen.....	6.66	7.04	—
Nitrogen	20.74	—	20.65

This substance crystallises in microscopic needles of a satiny aspect. It is a powerful electric. At a high temperature it decomposes before undergoing fusion. It is difficultly soluble in alcohol.

The *hydrochloride* contains two molecules of acid, and has therefore the composition C₁₅H₁₈N₄O.2HCl, as will be seen from the following analysis:—

- .1100 gram of substance gave—
 .2104 „ „ CO₂, and
 .0564 „ „ OH₂.

	Theory.	Experiment.
Carbon	52.48	52.16
Hydrogen	5.86	5.6

It is a white almost amorphous body. It forms a *platinum salt* corresponding with the hydrochloride, but it has not been obtained in a perfectly pure state.

One preparation gave 27.8 per cent. of platinum, the theory requiring 28.9 per cent.

LXV.—*Action of Heat on the Mixed Vapours of Benzene and Toluene. Two New Methylene-diphenyls.*

By THOS. CARNELLEY, D.Sc., Professor of Chemistry in Firth College, Sheffield.

IN a former communication (this Journal, 1876, i, 13) it has been shown that the hydrocarbon, paratolylphenyl, may be obtained by the action of sodium on a mixture of bromobenzene and parabromotoluene. The yield, however, was so small that the amount of pure compound obtained rendered it impossible to give more than a general description of the hydrocarbon and a few of its derivatives. With the view, therefore, of making a more complete study of this hydrocarbon, as well as of the homologous hydrocarbon ditolyl, both bodies have been prepared in much larger quantity and at much less cost, by the action of heat on a mixture of benzene and toluene, a reaction analogous to that by which diphenyl is obtained from benzene. The preparation of these hydrocarbons by this method has also induced me to make a more or less complete investigation of this reaction, which has not only given a very fair yield of both tolylphenyl and ditolyl, but has also led to the discovery of two new hydrocarbons, viz., γ - and δ -methylene-diphenylene.

The action of heat on various aromatic hydrocarbons has already formed the subject of several investigations by different chemists, especially Barbier, but it will be sufficient to refer to previous researches on the action of heat on benzene alone, toluene alone, and on a mixture of these two hydrocarbons.

Benzene.—(1.) In *Watts' Dict. of Chem.*, i, 542, it is stated that when the vapour of benzene is passed through a red-hot tube carbon is separated and a gaseous hydrocarbon formed. (2.) Berthelot (*Bull. Soc. Chim.* [2], 6, 272, 279) has shown that under these circumstances

benzene gives hydrogen, a little acetylene, diphenyl, chrysene, benzerhythrene, and a black pitchy substance, which he termed bitumene. (3.) Schultz (*Annalen*, 174, 201; this Journal, 1875, 151) states that when benzene is passed through a red-hot tube, the same bodies are obtained as mentioned by Berthelot, but finds that Berthelot's chrysene is a mixture of paradiphenylbenzene, isodiphenylbenzene, and a yellow oil, and that his benzerhythrene consists chiefly of diphenylbenzene, together with two hydrocarbons melting at 266° and 196° respectively. Schultz was unable to detect the presence of coal-tar chrysene as stated by Berthelot. (4.) Berthelot (*Bull. Soc. Chim.* [2], 22, 437; this Journal, 1875, 760) in his reply to Schultz, maintains that the chrysene which he obtained by the action of heat on benzene is an individual body identical with coal-tar chrysene, and that it is distinct from Schultz's diphenylbenzene, for it combines with picric acid, whereas the latter does not.

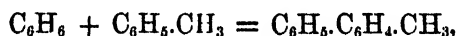
Toluene.—(1.) According to Berthelot (*Bull. Soc. Chim.* 1867, 1, 218), toluene, when passed through a porcelain tube heated to bright redness, gives uncondensable gases, benzene, naphthalene, dibenzyl, a hydrocarbon apparently isomeric therewith, anthracene, chrysene, and benzerhythrene. (2.) Graebe (*Ber.*, 1874, 48; this Journal, 1874, 471) finds that under these circumstances toluene gives benzene, diphenyl, anthracene, and phenanthrene, but no naphthalene or benzyltoluene. The chief product was a liquid boiling at 270 — 280° , and consisting probably of two ditolyls. (3.) Lorenz states (*Ber.*, 1874, 1097) that toluene by the action of heat in presence of lead oxide is converted into stilbene, diphenyl, phenanthrene, anthracene, and liquid hydrocarbons, probably ditolyl. Benzyltoluene and naphthalene could not be found.

Benzene and Toluene.—Barbier (*Ann. Chim. Phys.* [5], 7, 472; this Journal, 1877, i, 74) endeavoured to obtain fluorene (diphenylene-methane or methylene-diphenylene) by passing a mixture of benzene and toluene through a red-hot tube, but without any decisive result; a minute quantity of a body boiling near 301° and possessing fluorescent properties was formed, but the greater portion became converted into diphenyl and anthracene.

Judging from the above researches, the following bodies might be expected to be formed when a mixture of benzene and toluene is passed through a red-hot tube:—

		M. p.	B. p.
Hydrogen	H	—	—
Acetylene	C ₂ H ₂	—	—
Benzene	C ₆ H ₆	—	80
Naphthalene	C ₁₀ H ₈	79	218
Diphenyl	C ₁₂ H ₁₀	70	254
Two ditolyls.	C ₁₄ H ₁₄	?	?
Stilbene.	C ₁₄ H ₁₂	(115—118)	About 292
Phenanthrene.	C ₁₄ H ₁₀	100	340
Anthracene.	C ₁₄ H ₁₀	213	360
Chrysene.	C ₁₈ H ₁₂	<div style="display: inline-block; vertical-align: middle;"> { 200 230—235 250 275 } </div>	Above 360
Paradiphenylbenzene	C ₁₈ H ₁₄	205	Above 360
Isodiphenylbenzene	C ₁₈ H ₁₄	85	About 360
Hydrocarbon	?	196	?
Hydrocarbon	?	266	?
Bitumene	?	—	—

In the experiments to which the present communication refers, the benzene and toluene were mixed in molecular proportion so as to give the best yield of tolylphenyl, thus:—



and the mixture dropped into a red-hot iron tube from a tap-funnel attached to the turned-up end of the tube. The latter, 3 feet long, and $1\frac{1}{2}$ inch internal diameter, was filled with fragments of pumice-stone and laid in an ordinary combustion furnace, one end of which was slightly tilted up, so that the end of the tube bearing the tap-funnel was higher than the other; to this was fixed a glass tube leading to a well-cooled flask fitted with a condenser leading to a second flask. By this means the loss of any of the condensable products was avoided. The end of the iron tube remote from the tap-funnel was kept cool by tying round it a piece of cloth moistened by a continuous jet of cold water.

The furnace was maintained at a low red heat, and the mixed hydrocarbons passed through at the rate of about 80 grams per hour. When the whole had been passed through, the product obtained was distilled, and the portion boiling below 120° again passed through, the process being repeated ten times.

The benzene employed boiled at 80—85°, and the toluene at 105—115°, the total weight of the mixture taken for the experiment being 4,587 grams. The amount of action which occurred each time the mixture was passed through was as follows:—

	Per cent.	Mean. Per cent.
Unchanged hydrocarbons, b. p. 80—120°	84.4—91.9	89
Changed do. boiling above 120°..	3.9— 7.4	6
Loss and uncondensable gases	3.3— 8.2	5
		<hr/> 100

After passing through ten times (the changed portion being separated by distillation after each passage), the final result was as follows:—

	Grams.	Per cent.
Unchanged hydrocarbons, b. p. 80—120°	1769	39.1
Changed do. boiling above 120°	1453	32.1
Loss and uncondensable gases	1365	28.8
	<hr/> 4587	<hr/> 100.0

Though what is termed above “unchanged hydrocarbon,” consisted of benzene and toluene, it must not be supposed that the whole of it had absolutely undergone no change at all, for a certain portion of the benzene had really been produced from the toluene by the action of heat, Berthelot and Graebe (*loc. cit.*) having shown that toluene, under these circumstances, is partially converted into benzene.

In order to ascertain the relative proportion of benzene and toluene in this “unchanged hydrocarbon” remaining at the end of the experiment, it was subjected to fractionation, with the following results:—

		After action. Per cent.	Before action. Per cent.
Benzene, b. p. 80—87°	1088	24	18
Toluene, b. p. 105—115°	681	15	21
	<hr/> 1769	<hr/> 39	<hr/> 39

so that after the action of heat the hydrocarbons were present in the proportion of 24 to 15, whilst before the action the proportion was 18 to 21. This is due partly to the toluene being more easily acted on than benzene, and partly to the fact that toluene gives benzene as well as other products when exposed to a red heat.

The “loss” is chiefly due to the formation of uncondensable gases, hydrogen, acetylene, &c.

The total changed hydrocarbons, amounting to 1,453 grams, were then submitted to a systematic fractionation, as follows. For the measurement of temperatures above 300° the method described by Mr. Williams and myself (this Journal, 1878, 33, 281) was employed, which consisted in placing capillary tubes containing metallic

salts of known melting point in the vapour of the boiling hydrocarbon.

Fraction.	Weight of fraction.	Remarks.
120—190.....	29	Liquid.
190—245.....	1	Solid.
{ 245—258.....	499	Solid. }
{ 245—258.....	5	Liquid. }
258—263.....	25	Liquid, with very little solid.
263—269.....	231	Liquid.
269—272.....	55	Liquid.
272—280.....	104	Liquid, nearly all at 272—276.
280—293.....	31	Liquid, with a little solid.
293—305.....	36	Nearly all solid.
305—316.....	10·5	All solid.
316—339.....	24·5	
339—359.....	22·5	
359—383.....	15·5	
383—404.....	12·0	
404—427.....	65·0	
427—439.....	19·0	
Above 439	71·0	
Loss and small portion below 120°.....	197·0	
	<hr/> 1453·0	

From the above it is seen that the products formed in largest quantity are those boiling at 245—258° (diphenyl, b. p. 254°), at 263—269° (paratolylphenyl, b. p. 263—267°), at 272—280° (ditolyl, b. p. 270—280°), at 404—427° (paradiphenyl-benzene, b. p. 404—427°), and bituminous bodies boiling above 439°.

Each of the above fractions was then examined separately, and the constituent hydrocarbons isolated as far as possible in the pure state by the combined assistance of fractionation, crystallisation of the solid from the liquid portions in a freezing mixture of salt and ice, and recrystallisation from alcohol, benzene, &c. The more important fractions gave the following results:—

Fraction 120—190 consisted of toluene.

Fraction 190—245 gave naphthalene.

Fraction 245—258 gave diphenyl.

Fraction 263—269 gave paratolylphenyl.

Fraction 272—280 gave orthoparaditolyl.

Fraction 293—305 gave the new hydrocarbon γ -methylene diphenylene, a little phenanthrene, and an oil.

Fraction 305—316 gave the new hydrocarbon δ -methylene diphenylene, phenanthrene, and an oil.

Fraction 316—339 gave δ -methylene diphenylene, a very little diphenylbenzene, phenanthrene, and an oil.

Fraction 339—359 consisted chiefly of an oil with a little diphenylbenzene.

Fraction 359—383 gave anthracene, diphenylbenzene, and an oil.

Fraction 383—404 gave anthracene, diphenylbenzene, and an oil.

Fraction 404—427 consisted of diphenylbenzene, an oil, a hydrocarbon having the composition $C_{32}H_{28}$, and a semi-solid portion which on oxidation with chromic and glacial acetic acids gave a small quantity of paradiphenyl-carboxylic acid, and a quinone which blackens at 260° , but does not completely melt at 310° .

Fraction 427—439 on exhaustion with boiling alcohol gave an insoluble black bitumen, becoming solid and brittle on cooling, a small quantity of nearly insoluble diphenylbenzene, and a difficultly soluble reddish oil, which formed the chief portion.

Fractions above 439, and which remained behind in the still, consisted of a solid black bitumen.

The several hydrocarbons isolated from the above fractions were identified as follows:—

Naphthalene, $C_{10}H_8$, obtained from the solid fraction 190—245, was recrystallised from alcohol, when the m. p. = $72-76^\circ$, and b. p. = 213° uncorr., 217° cor.; after sublimation the m. p. = 79.5° . It sublimed in beautiful plates, and had the characteristic smell of naphthalene, which melts at 79.5° , and boils at $217-218^\circ$ (Vohl, *J. pr. Chem.*, **102**, 29).

Diphenyl, $C_{12}H_{10}$, after recrystallisation twice from alcohol melted at 70° , and boiled at $245-258^\circ$: pure diphenyl melts at 70° , and boils at 254° (Schultz, *Annalen*, **174**, 205; according to Christomanos, *Gazzetta*, 1875, 402, it melts at 69.6° and boils at 238.5°). The dibromide was prepared, and on analysis gave the following numbers:—

- (1.) 0.1985 gram of substance gave 0.2305 gram AgBr, and 0.0048 gram Ag = 51.2 per cent. Br.
- (2.) 0.2346 gram of substance gave 0.2700 gram AgBr, and 0.0077 gram Ag = 51.4 per cent. Br.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
$C_{12}H_8Br_2$	51.28	51.20	51.40	51.30

The melting point of this dibromide = 162° (164° , "Schorlemmer's Chemistry of the Carbon Compounds").

(1.4) *Paratolylphenyl*, $Me.C_6H_4.Ph$.—This hydrocarbon, after distil-

lation over sodium, formed a colourless refractive liquid boiling at 263—268° (paratolylphenyl from the action of sodium on mixed bromobenzene and parabromtoluene boils at 263—267°, Carnelley, this Journal, 1876, 29, 16), and on analysis gave the following:—

Weight taken.....	0.1764	
H ₂ O obtained	0.1129 =	7.11 per cent. H.
CO ₂ „	0.5955 =	92.07 per cent. C.
	Calculated.	Found.
C ₁₃	92.86	92.07
H ₁₂	7.14	7.11

Two vapour-density determinations by Victor Meyer's method gave—

	(1.)	(2.)
Weight taken.....	0.030 gram.	0.0415 gram.
Volume of gas	4.4 c.c.	5.6 c.c.
t	14° C.	14° C.
Barometer	757 mm. at 13° C.	757 mm. at 12.2° C.

	Calculated for C ₁₃ H ₁₂ .	Found.		
		(1.)	(2.)	Mean.
Vapour-density (H = 1)....	84	82	89	85.5

The hydrocarbon on oxidation with chromic and glacial acetic acids gave first paradiphenyl-benzoic acid, C₆H₄.Ph.COOH, melting at 216—220° (216—217°, Schultz, *Annalen*, 174, 213; 218—219°, Doebner, *ibid.*, 172, 112), and then terephthalic acid.

The monobromide, C₁₃H₁₁Br, obtained by the action of the calculated quantity of bromine on the hydrocarbon, crystallises from alcohol in pearly plates (m. p. 127—129°, resolidifies at 123°) exactly resembling those (m. p. 130—131°, resolidifies at 121°) obtained from the tolylphenyl resulting from the action of sodium on the mixed bromides of benzene and toluene.

The analysis of the hydrocarbon b. p. 263—268°, its vapour-density, the products of its oxidation, and the formation of the monobromide, together with its general properties, prove it to be (1.4) paratolylphenyl, identical with that obtained from the mixed bromides by the action of sodium.

(1.2, 1.4) *Orthoparaditolyl*, Me.C₆H₄.C₆H₄.Me, boils at 272—280°, and on oxidation with chromic and glacial acetic acids gives first (1.2 1.4) orthoparatolylphenyl carbonic acid, Me.C₆H₄.C₆H₄.COOH (m. p. 179—180°), and finally terephthalic acid. On analysis the following numbers were obtained:—

	(1.)	(2.)
Weight taken....	0.2020 gram.	0.1865 gram.
CO ₂ obtained	0.6780 „	An accident to the potash bulbs prevented the determination of the C in this case.
H ₂ O obtained....	0.1370 „	0.1300 gram.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
C ₁₄	92.31	91.54	—	91.54
H ₁₄	7.69	7.54	7.74	7.62

Two vapour-density determinations gave as follows:—

	(1.)	(2.)
Weight taken ..	0.0385 gram.	0.0400 gram.
Volume of gas..	4.81 c.c.	5.3 c.c.
<i>t</i>	11° C.	13° C.
Barometer.....	755.6 mm. at 10°	757 mm. at 11.7°.

	Calculated for C ₁₁ H ₁₄ .	Found.		Mean.
		(1.)	(2.)	
Vapour-density (H = 1)..	91	95	90	92.5

This hydrocarbon is therefore identical with the orthoparatolyl-phenyl (b. p. = 270—280°) which is obtained by the action of sodium on bromtoluene, and on oxidation gives first orthoparatolylphenyl-carboxylic acid (m. p. 176°), and finally terephthalic acid (Carnelley, this Journal, 1877, ii, 655). No solid (dipara-) ditolyl was produced by the action of heat on the mixed vapours of benzene and toluene. Only a very small quantity is obtained by the action of sodium on bromtoluene (Zincke, *Ber.*, 4, 396).

γ-Methylene-diphenylene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$.—This new hydrocarbon was

obtained from the fraction boiling at 293—305° by pressing out the only portion between filter-paper, and crystallising the solid portion repeatedly from alcohol. It crystallises in small pearly plates, which melt at 118°, resolidify at 116°, and boil at 295° (uncorr.). It is moderately soluble in hot alcohol and hot glacial acetic acid, but only sparingly soluble in cold alcohol, or in cold glacial acetic acid; it is easily soluble in ether. Its alcoholic and acetic acid solutions possess a faint blue fluorescence. In one case it was obtained crystallised in small needle-shaped prisms. It gave the following on analysis:—

	(1.)	(2.)
Weight taken....	0·2450 gram.	0·1932 gram.
CO ₂ obtained....	0·8433 „	An accident to the potash bulbs prevented the determination of the C in this case.
H ₂ O obtained....	0·1346 „	0·1100 gram.

	Calculated.	Found.		Mean.
		(1.)	(2.)	
C ₁₃	93·99	93·87	—	93·87
H ₁₀	6·01	6·10	6·33	6·21

The vapour-density was determined as follows:—

	(1.)	(2.)
Weight taken ..	0·0355 gram.	0·0355 gram.
Volume of gas ..	5·1 c.c.	5·0 c.c.
t	14° C.	14° C.
Barometer	755·6 mm. at 11·7°	758·9 mm. at 12·2°.

	Calculated for C ₁₃ H ₁₀ .	Found.		Mean.
		(1.)	(2.)	
Vapour-density (H = 1)..	83	83·8	85·0	84·4

The *picrate*, C₁₃H₁₀.C₆H₃(NO₂)₃O, was prepared by dissolving the calculated quantities of the two compounds separately in ether, mixing, and leaving the mixture to evaporate spontaneously. It crystallises in splendid blood-red needles, melting at 79—81°, to a dark blood-red liquid.

γ-Methylene-diphenylene quinone, C₁₃H₈O₂, was obtained by oxidising the hydrocarbon with chromic and glacial acetic acids. The white curdy precipitate produced on dilution with water was filtered off and treated with warm ammonia to separate any acid, and filtered. The ammoniacal filtrate did not give the least precipitate on addition of hydrochloric acid, showing the absence of any insoluble acid as the product of oxidation. The yellow body insoluble in ammonia was crystallised from alcohol in the form of long golden-yellow needles (m. p. 280—281°, corr.), which were scarcely soluble in cold, and only sparingly soluble in hot alcohol. It sublimes when heated on a watch-glass without previous melting. An analysis gave the following:—

Weight taken	0·0840 gram.	
CO ₂ obtained.....	0·2435 „	= 79·06 per cent. C.
H ₂ O „	0·0340 „	= 4·49 per cent. H.

	Calculated.	Found.
C ₁₃	79.59	79.06
H ₈	4.08	4.49
O ₂	16.33	16.45
	100.00	100.00

The hydrocarbon when treated with a large excess of chromic acid was oxidised entirely to carbonic anhydride and water, but in no case was any diphenylene ketone obtained.

Dibromo-γ-methylene-diphenylene, C₁₃H₈Br₂, was obtained by adding gradually an excess of bromine to an ethereal solution of the hydrocarbon. The liquid became warm, but no precipitate separated (in this respect differing from stilbene). After slight evaporation and standing it became a mass of white crystals; these (A) were filtered off from the solution (B), washed with ether and dried; under the microscope they appeared to consist of octohedrons mixed with a few needles. They were boiled with ether and then consisted entirely of octohedrons (m. p. 157°, s. p. 149°); the ethereal solution on evaporation gave crystals consisting at first entirely of needles, but these on standing and drying changed to octohedrons (m. p. 162°, s. p. 149°). The original ethereal mother-liquor (B) on evaporation gave crystals consisting entirely of octohedrons (m. p. 162°, s. p. 149°). Dibrom-γ-methylene-diphenylene crystallises therefore either in needles or octohedrons, the latter being the more stable form, the acicular always changing into the octohedral form in course of time. It melts at 162° and resolidifies at 149°; it is but very sparingly soluble in alcohol or ether whether hot or cold. On analysis it gave:—

0.2255 gram of substance, gave 0.202 gram AgBr, and 0.0354 gram Ag = 49.74 per cent. Br.

	Calculated for C ₁₃ H ₈ Br ₂ .	Found.
Br ₂	49.38	49.74

δ-Methylene-diphenylene, $\begin{array}{c} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{array} \text{CH}_2$. This new hydrocarbon occurred

in the fractions boiling at 305—339°. It formed the portion of those fractions least soluble in alcohol, and was therefore obtained pure by repeated crystallisation from that solvent. It crystallises in small pearly plates, which are only sparingly soluble in cold, but more easily in hot alcohol. It melts at 205° uncorr., 208° corr., and boils at about 320°. An analysis gave the following results:—

Weight taken	0.135 gram.		
CO ₂ obtained.....	0.464	,,	= 93.74 per cent. C.
H ₂ O ,,	0.074	,,	= 6.09 per cent. H.

	Calculated.	Found.
C ₁₃	93·99	93·74
H ₁₀	6·01	6·09

Two vapour-density determinations gave as follows:—

	(1.)	(2.)
Weight taken....	0·0185 gram.	0·0250 gram.
Volume of gas....	2·65 c.c.	3·7 c.c.
<i>t</i>	20° C.	20° C.
Barometer	746·8 mm. at 19°	746·8 mm. at 19°.

	Calculated. for C ₁₃ H ₁₀ .	Found.		Mean.
		(1.)	(2.)	
Vapour-density (H = 1)..	83	87·7	84·8	86·2

This hydrocarbon is probably identical with Linnemann's (*Annalen*, **133**, 1) benzhydrolene (C₁₃H₁₀), which he obtained by the distillation of the succinate or benzoate of benzhydrol. Benzhydrol has the constitution C₆H₅.CHOH.C₆H₅, being obtained from benzophenone by the action of nascent hydrogen. Benzhydrolene melted at 209—210°, was nearly insoluble in alcohol even on boiling, from which it crystallised in small needles, sparingly soluble in ether, but easily in hot benzene. It did not appear to combine with picric acid.

δ-Methylene-diphenylene quinone, C₁₃H₈O₂, was obtained by oxidising the hydrocarbon with chromic and glacial acetic acids. On addition of water the quinone was thrown down as a white precipitate, which was perfectly insoluble in ammonia. It is a pure white powder, which sublimes in needles and melts at 276—277° uncorr., 288° corr. (another sample melted at 277—278° uncorr.), to a yellowish-green fluorescent liquid, resembling uranium glass, except that the green is rather more decided. It is insoluble in water, but moderately soluble in glacial acetic acid. An analysis gave the following numbers:—

0·0672 gram substance gave 0·1970 gram CO₂, and 0·0272 gram H₂O = 79·95 per cent. C and 4·49 per cent. H.

	Calculated.	Found.
C ₁₃	79·59	79·95
H ₈	4·08	4·49
O ₂	16·33	15·56
	100·00	100·00

The formation of a diphenylene ketone was not observed.

Phenanthrene, C₁₄H₁₀, was found in those solid portions of the fractions 293—339°, which were most easily soluble in alcohol. It was recognised as follows:—It fused at 101° (100°, Graebe, *Ber.*, **5**, 861;

99—100°, Fittig and Ostmeyer, *ibid.*, 5, 933) and resolidified at 92°. It crystallised in small pearly white plates, which were easily soluble in hot and moderately soluble in cold alcohol. On oxidation with chromic and glacial acetic acids it gave phenanthraquinone, $C_{14}H_8O_2$, which crystallised from alcohol in orange-yellow needles, melting in one case at 203—205° and in another at 201° (205°, "Schorlemmer's Chemistry of the Carbon Compounds;" 202°, Limpricht, *Ber.*, 6, 533; 198°, Graebe, *Ber.*, 5, 861; 198, Fittig and Ostmeyer, *Ber.*, 5, 933). The quinone combined with acid sodium sulphite, from which it was precipitated by hydrochloric acid; the solution in acid sodium sulphite, on standing in contact with sulphurous acid, was converted into the dark-brown quinhydrone.

Anthracene, $C_{14}H_{10}$, occurred in the fractions 359—404°, and was separated from the admixed diphenylbenzene by boiling repeatedly with alcohol, in which the latter is insoluble. On oxidation with chromic and glacial acetic acids it gave anthraquinone, $C_{14}H_8O_2$, crystallising from hot alcohol in pale-yellow needles, which melt at 273—274° (273°, *Watts' Dict. Chem.*, 6, 180), and are only very sparingly soluble in hot alcohol.

(1.4) *Paradiphenylbenzene*, $C_6H_4Ph_2$, was found in the fractions 316—439°, but chiefly in that boiling at 404—439°. It is isolated by exhausting the several fractions with boiling alcohol, when it remains behind insoluble. It was further purified by crystallising several times from benzene. It crystallised in needles and sublimed in iridescent laminae, which melted at 205—207° uncorr., 212—213° corr. (another sample gave 206—208° uncorr.), and boiled* at 404—427° (m. p. 206°, Barth and Schreder, *this Journal*, 1879, xxxvi, 66; m. p. 201° uncorr., 205° corr., boils in the vapour of boiling sulphur at 440°, Riese, *Zeits. f. Chem.* [2], 6, 192, 735; m. p. 205°, b. p. above 360°. Schultz, *Ber.*, 6, 415; b. p. about 400°, "Schorlemmer's Chemistry of Carbon Compounds"). It was insoluble in water and almost perfectly insoluble in alcohol; very sparingly soluble even in boiling glacial acetic acid, and separated therefrom in small iridescent laminae. It was moderately soluble in benzene, the solution possessing a blue fluorescence, and crystallised therefrom in pearly plates, which adhered together and exhibited a greenish reflection, but became white on drying at 120°. It was easily soluble in carbon bisulphide, and in this solvent was not perceptibly attacked by bromine. An analysis of the hydrocarbon dried at 120° gave as follows:—

Weight taken	0.237	gram.	
CO ₂ obtained	0.811	„	= 93.33 per cent. C.
H ₂ O „	0.1335	„	= 6.26 per cent. H.

* Between the melting points of $Tl_{12}V_{10}O_{31}$ (m. p. 404°) and $TlCl$ (m. p. 427°)
See *this Journal*, 1878, 33, 277.

	Calculated.	Found.
C ₁₈	93.91	93.33
H ₁₄	6.09	6.26

A vapour-density determination gave:—

Weight taken	0.034 gram.*
Volume of gas.....	3.7 c.c.
t.....	16° C.
Barometer.....	757 mm. at 16.9°.

	Calculated for C ₁₈ H ₁₄ .	Found.
Vapour-density (H = 1).....	115	111.6*

This hydrocarbon did not combine with picric acid, and dissolved in strong sulphuric acid on warming, first with a dirty green colour, changing to a dirty blue, and finally on boiling to purple. On oxidation with a deficit of chromic and glacial acetic acids it gave a white acid which fused at 216° uncorr., and formed a white silver salt, an analysis of which gave:—

0.080 gram of substance gave 0.0283 gram Ag = 35.37 per cent. Ag.

	Calculated for C ₁₃ H ₉ O ₂ Ag.	Found.
Ag	35.41	35.37

The acid was therefore paradiphenylcarboxylic acid, which, according to Doebner (*Annalen*, **172**, 112), melts at 218—219°, and according to Schultz (*Annalen*, **174**, 213) at 216—217°. On oxidation with excess of chromic acid the hydrocarbon gave terephthalic acid. The above facts prove that this hydrocarbon is paradiphenylbenzene, and identical with that obtained by Riese (*Zeits. f. Chem.* [2], **6**, 192) from the action of sodium on an ethereal solution of solid dibromobenzene and monobromobenzene, and also with that obtained by Schultz (*Ber.*, **7**, 1365), by passing benzene through a red-hot tube.

I was unable to detect the presence of the isodiphenylbenzene (m. p. 85°) said by Schultz to be produced at the same time as the above isomer (m. p. 205—207°), though it is very probable that its isolation in the present case was prevented by its mixture with other hydrocarbons of nearly equal solubility.

The Hydrocarbon, C₃₂H₂₈, which apparently occurred in fraction 404—427°, could not be isolated in the pure state. It was more soluble in alcohol than paradiphenylbenzene, and on oxidation with chromic and glacial acetic acids it gave a quinone, which crystallised

* Barth and Schreder also found 111.5 (H = 1) by Meyer's method; this *Journal*, 1879; xxxvi, 66.

from alcohol in orange-red needles (m. p. 180°). This quinone is insoluble in water, but moderately soluble in alcohol, forming a dark red-brown liquid. It dissolves in strong sulphuric acid with a brown colour, which did not change on boiling. An analysis gave:—

Weight taken.....	0.071 gram.		
CO ₂ obtained.....	0.226 „	=	86.81 per cent. C.
H ₂ O obtained.....	0.038 „	=	5.94 per cent. H.
	Calculated.		Found.
C ₂₃	86.88		86.81
H ₂₆	5.88		5.94
O ₂	7.24		7.25
	<hr/> 100.00		<hr/> 100.00

The bitumene from fraction 427— 439° consisted of a solid black mass with a conchoidal fracture. It was insoluble in alcohol and glacial acetic acid, but easily soluble in carbon bisulphide and in benzene, and moderately soluble in ether. No definite compound could be isolated from it either by the use of solvents or by combination with picric acid. On oxidation with chromic and glacial acetic acids, to which a little benzene had been added to increase the solvent power, it was burnt almost completely to carbonic anhydride and water, the liquid on dilution with water giving only a very small precipitate. This precipitate, by treatment with ammonia, was separated into a small quantity of an acid and a quinone. The acid after crystallisation from alcohol melted about 280° , but the quantity was so small that it could not be obtained in the pure state. The yellow quinone, which melted only partially at 340° , dissolved in alcohol, forming a yellow liquid, with a beautiful green fluorescence. The quantity obtained, however, was too small to work with.

The bitumene boiling above 439° was a solid black mass with conchoidal fracture. It was scarcely at all soluble in benzene, but much more easily in carbon bisulphide; very sparingly soluble in glacial acetic acid with a yellowish-green fluorescence. It first showed signs of melting at 190° , began really to melt at about 220° , but was not completely fused even at 320° . It melted completely when heated in capillary tubes directly over the lamp. It burnt with a smoky flame, but was at once extinguished on removing from the lamp flame. On oxidation with chromic and glacial acetic acids (with addition of a little benzene) the portion attacked was burnt completely to carbonic anhydride and water.

The oils from the several fractions 293— 439° were cooled in a freezing mixture to separate solid hydrocarbons and submitted to a

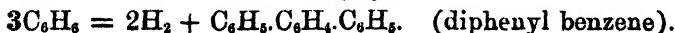
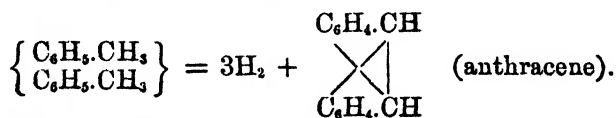
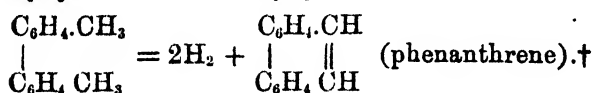
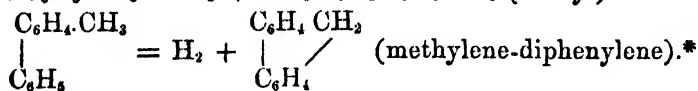
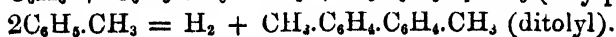
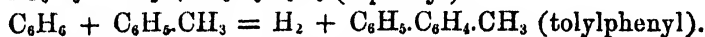
systematic fractionation, when they distilled almost completely in three different portions, viz. :—

(A) 293—316° (B) 359—383° (C) 404—427°.

These are still under investigation. The fraction (A) appears to be a nearly pure compound; after distillation over sodium it forms a pale yellow oil, which solidifies at -10° and melts at about $+13^{\circ}$.

From the above we may conclude, therefore, that when the mixed vapours of benzene and toluene are passed through a red-hot tube, the following hydrocarbons are formed:—Benzene, naphthalene, diphenyl, paratolylphenyl, orthoparaditolyl, γ -methylene-diphenylene, δ -methylene-diphenylene, phenanthrene, anthracene, paradiphenylbenzene, a hydrocarbon having the formula $C_{22}H_{28}$, a liquid hydrocarbon boiling at 293—316°, and melting at 13° , two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359—383° and 404—427° respectively, and a solid black bitumene.

The more important changes occurring during this reaction may be represented as follows :—



The γ - and δ -methylene-diphenylenes described above are isomeric, and not identical, with the methylene-diphenylene \ddagger obtained by Graebe (*Annalen*, 174, 194) by passing diphenylmethane through a red-hot tube; and by Fittig (*Ber.*, 6, 187) by the reduction of diphenylene ketone with zinc-dust, or with hydriodic acid and amorphous phosphorus; or with the fluorene \S discovered by Berthelot (*Ann. Chim. Phys.* [4], 12, 222) in the portion of coal-tar boiling at 300—

* Compare Barbier (*Ann. Chim. Phys.* [5], 7, 472; this Journal, 1877, 1, 74.

† Compare Barbier (*Compt. rend.*, 79, 121; this Journal, 1874, 1091.

‡ This may be distinguished as α -methylene-diphenylene; Graebe called his compound *diphenylene-methane*.

§ This may be called β -methylene-diphenylene.

400°, and more fully examined by Barbier (*ibid.* [5], 7, 472). More recently the methylene-diphenylene from diphenylene ketone has been re-examined by Fittig and Schmitz (*Annalen*, 193, 134), who have obtained it in large quantity, and consider that they have shown it to be identical in all respects with coal-tar fluorene. The following table (p. 717) exhibits the more important properties of the several diphenylene methanes.

This table shows: (1) that the δ -compound is undoubtedly different from the other three. (2) That the γ -compound is also distinct from Graebe's and Berthelot's hydrocarbons, as is proved by its higher melting point, by the fact that it does not give the least trace of diphenylene ketone, but a quinone (melting at 280°) on oxidation, and by the melting point of its dibromide. It also differs from the α -compound in the very sparing solubility of its dibromo-derivative in ether, that of the former compound being very easily soluble in this solvent.

The only question that remains is the identity or non-identity of coal-tar fluorene and the methylene-diphenylene from diphenylene ketone. As already mentioned, Fittig and Schmitz believe that the two are identical, and that the difference in properties is due to the fluorene examined by Barbier being contaminated with small quantities of other hydrocarbons. Watts (*Dict. of Chem.*, 8, 797) suggests that Barbier's fluorene was a mixture of two isomeric methylene-diphenylenes, one of which was identical with Graebe's hydrocarbon. If this supposition be correct the admixed hydrocarbon cannot be either the γ - or the δ -compound described above, as Barbier's quinone melted at 181—182°, whilst the quinones from the latter hydrocarbons fused at 280° and 288° respectively. In view of the formation of the two new methylene-diphenylenes, both of which give a quinone on oxidation, it is thought to be more probable that coal-tar fluorene is isomeric and not identical with Graebe's methylene-diphenylene from diphenylene ketone, the chief points of distinction between the two being (1) the much stronger fluorescence of coal-tar fluorene; (2) the colour and melting points of the dinitro-compounds, the one being colourless and melting at 200°, and the other reddish-yellow and melting above 260°; (3) on oxidation the one gives a ketone only, and the other a ketone (m. p. 81—82°) and a quinone; (4) the dibromide of the one melts at 153° (Graebe), at 162—167° (Fittig and Schmitz), and is easily soluble in ether, whilst that of the other melts at 166—167°, and is nearly insoluble in ether.

The compound, $C_{15}H_8O_2$, obtained by Behr and v. Dorp (*Ber.*, 7, 398), together with diphenylene oxide, by the action of lead oxide on phenol is probably identical with Barbier's methylene-diphenylene quinone. It melts at 173—174°.

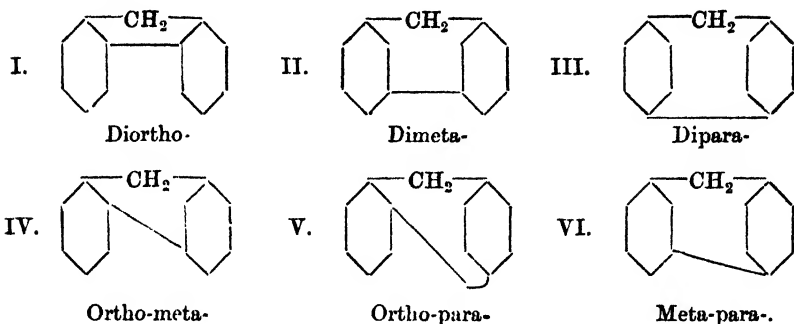
If then all these four methylene-diphenylenes are distinct, what is

	α -Methylene-diphenylene from diphenylmethane and diphenylene ketone (Graebe, Fittig, and Schmitz).	β -Methylene-diphenylene or coal-tar fluorene (Ber- thelot; Barbier).	γ -Methylene-diphenylene. From benzene and toluene (Carnelley).	δ -Methylene-diphenylene.
Melting point .. {	113–114° (Graebe), 112– 113° (Fittig and Schmitz)	113°.	118° (uncorr.).	205° (uncorr.), 208° (corr.).
Boiling point .. {	300–305° (Graebe); 294– 295° (Fittig and Schmitz).	About 305° (corr.).	295° (uncorr.).	About 320°.
Crystalline form {	Colourless laminae with faint blue fluorescence.	Sublimes in plates with strong violet fluorescence.	Colourless pearly plates or small needle-shaped prisms, with very faint blue fluores- cence.	Small colourless pearly plates.
Solubility	Easily in hot alcohol. Less soluble in cold alcohol, very easily in carbon bisulphide, ether, and benzene.	Very soluble in ether, ben- zene, carbon bisulphide, and hot alcohol, but only spar- ingly soluble in cold alco- hol.	Moderately soluble in hot alcohol or hot glacial acetic acid, but only sparingly soluble in cold alcohol or cold glacial acetic. Easily in ether.	Sparingly soluble in cold, but more easily in hot alcohol.
Picrate	Yellow-red or red needles, m. p. = 80–82°, very easily soluble in alcohol, but de- composed at same time (Graebe). Red - brown prisms, m. p. = 79–80° (Fittig and Schmitz).	Red needles, m. p. 80–82°.	Blood-red needles, m. p. = 79–81°.	—

	α -Methylene-diphenylene from diphenylmethene and diphenylene ketone (Graebe, Fittig, and Schmitz).	β -Methylene-diphenylene or coal-tar fluorine (Ber- thelot; Barbier).	γ -Methylene-diphenylene. From benzene and toluene (Carnelley).	δ -Methylene-diphenylene.
Dibromo-com- pound	Colourless tabular mono- clinic prisms, different in form from those of Barbier; m. p. = 162–167° (Fittig and Schmitz). Needles, m. p. 153–154° (Graebe), very sparingly soluble in alcohol, very easily in ether, benzene, carbon bisulphide and chloroform.	Monoclinic crystals, m. p. = 166–167°. Nearly insolu- ble in ether and alcohol, but readily soluble in car- bon bisulphide and chloro- form. They change on repeated crystallisation from carbon bisulphide into the same form as those of Fittig and Schmitz.	Minute octohedrons or needles, the latter changing into the former. M. p. = 162°. Very sparingly solu- ble in alcohol or ether, whether hot or cold.	—
Dinitro-com- pound	Colourless needles, m. p. 199 – 201°, very slightly soluble in hot alcohol.	Reddish-yellow needles, m. p. = above 260° with decon- position, very slightly solu- ble in ordinary solvents.	—	—
Oxidation pro- ducts	Is oxidised with difficulty, and gives only diphenylene ketone.	Is slowly oxidised, giving di- phenylene ketone and a quinone, $C_{13}H_9O_2$, m. p. = 181–182°.	Gives only a quinone and no ketone. The quinone, $C_{13}H_9O_2$, crystallises in golden-yellow needles, m. p. = 280–281°. Scarcely soluble in cold, and only sparingly soluble in hot alcohol.	Gives only a quinone and no ketone. The quinone, $C_{13}H_9O_2$, is a pure white powder, subliming in needles (m. p. 288°). Insoluble in water, but moderately solu- ble in glacial acetic acid.

their constitution? According to theory six modifications of the

formula, $\begin{matrix} \text{C}_6\text{H}_4 \\ | \\ \text{C}_6\text{H}_4 \end{matrix} \text{CH}_2$, are possible, viz. :—



Though the data at hand are far from conclusive, yet it is most probable that the α -, β -, γ -, and δ -methylene-diphenylenes have the constitutions I, IV or V, II, and III respectively, and for the following reasons :—

α -Methylene-diphenylene is obtained from diphenylene ketone, and α -methylene-diphenylene likewise forms diphenylene ketone on oxidation. Now diphenylene ketone is a diortho-compound, because it is produced by heating diphenic acid with lime, and diphenic acid is a diortho-compound, being derived from phenanthrene. α -Methylene-diphenylene is therefore almost certainly the diortho-modification. This is further confirmed by the fact that phenanthraquinone on heating with pure soda lime gives methylene-diphenylene (Anschütz and Schultz, *Ber.*, 9, 140). Anschütz and Japp (*Ber.*, 11, have also shown that diphenylene ketone gives phthalic acid on oxidation, and therefore that the CO-group in diphenylene ketone is in the diortho-position.

δ -Methylene-diphenylene obtained by the action of heat on benzene and toluene is almost certainly the dipara-derivative, for not only does it melt and boil above any of the other three modifications, but it melts very much higher, viz., at 205° , the next highest being the γ -modification, which melts at 118° . Now it is a general rule that the melting points of those compounds, the atoms of which are symmetrically arranged, are higher than in the case of isomeric compounds in which the atomic arrangement is less symmetrical (compare *Watts' Dict. Chem.*, 8, 221; Carnelley, *Phil. Mag.*, 1879, 378). Of the six possible constitutions for methylene-diphenylene, the dipara is the most symmetrical, and therefore the δ -modification with the highest melting point has most probably that constitution.

γ-Methylene-diphenylene. — Since this modification melts (118°) higher than the (α -) diortho-compound (113°), it is improbable that it would have a less symmetrical constitution, in which case it must be the dimeta-derivative.

β-Methylene-diphenylene. — Data are almost altogether wanting in order to decide which of the three remaining constitutions belongs to this compound (if it be really different from the α -modification), but as it forms a ketone as well as a quinone, it is not unlikely that one of the attachments is in the ortho-position, in which case it would be either the ortho-meta- or the ortho-para-compound.

General Results.

1. When the mixed vapours of benzene and toluene are passed through a red-hot tube, there are obtained benzene, naphthalene, diphenyl, paratolylphenyl, orthoparaditolyl, γ -methylene-diphenylene, δ -methylene-diphenylene, phenanthrene, anthracene, paradiphenyl benzene, a hydrocarbon having the composition $C_{32}H_{28}$, a liquid hydrocarbon boiling at 293 — 316° and melting at 13° , two other liquid hydrocarbons or mixtures of hydrocarbons boiling at 359 — 383° and 404 — 427° respectively, and a solid black bitumene.

2. Two new methylene-diphenylenes and some few of their derivatives are described.

3. Of the six possible methylene-diphenylenes three, and probably four are known.

4. Graebe and Fittig's methylene-diphenylene obtained from diphenylmethane and from diphenylene ketone is a diortho-compound; of the two modifications obtained by the action of heat on mixed benzene and toluene vapours, the one melting at 205° is the dipara-, and that melting at 118° is possibly the dimeta-modification; whilst Berthelot's coal-tar fluorene is probably either the ortho-meta- or the ortho-para-compound.

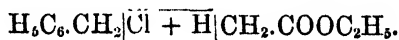
LXVI.—CONTRIBUTIONS FROM THE LABORATORY OF THE
ROYAL COLLEGE OF CHEMISTRY, SCIENCE SCHOOLS,
SOUTH KENSINGTON.

On the Action of Benzyl Chloride on Phenyl Acetate.

By W. H. PERKIN, Junior Assistant, and W. R. HODGKINSON,
Ph.D., F.I.C., &c., Chemical Demonstrator.

IN the course of some experiments on ethereal salts of acids of the fatty series, it occurred to one of us to examine the action of benzyl chloride on bodies of this class.

For this we chose at first ethyl acetate, with which it was possible that benzyl chloride might react in the same way as hydrogen chloride, or that the chlorine would remove hydrogen from the methyl group of the acetic acid in the sense of the expression—



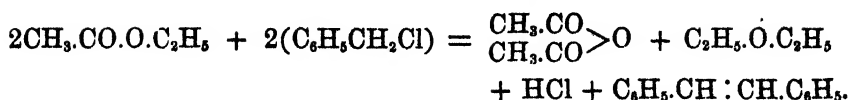
We tried this by sealing up equivalent quantities of the two substances, both most carefully dried, in glass tubes, and heating to about 150°.

The reaction must have been very violent, as most of the tubes burst after about 30 minutes at this temperature, enormous quantities of gaseous hydrogen chloride being liberated. The operation was then performed in a copper cylinder digester, and the contents, after letting off the large quantity of hydrogen chloride, distilled, when a small amount of distillate was obtained under 100° and a considerable quantity at about 130°, the thermometer afterwards rising rapidly to about 300°.

The 130° fraction exhibited every character of acetic anhydride. It was converted into the acid and identified beyond doubt. The amount of the fraction under 100° was too small to analyse, but appeared to be ether.

After several distillations, the oil boiling about 300° gave a fraction between 300° and 320°, which solidified, and after solution in alcohol and boiling with animal charcoal, several times repeated, gave crystals melting at about 116°.

The process of purification had so diminished the quantity that it was not sufficient for a combustion, but the long thin crystals and the approximation to the melting point seem to indicate that the body is stilbene, the reaction probably being—



With benzyl acetate and benzyl chloride some acetic anhydride was also produced, but the other products were less inviting than with the ethyl acetate.

We therefore confined our attention to its action on phenyl acetate, which we found could be carried on by heating the two liquids in a flask or retort with inverted condenser for some days.

About 3 kilos. of a mixture of equal parts of benzyl chloride and phenyl acetate, both quite pure and dry, were boiled in retorts, so arranged that the neck could be attached to a Bunsen water-pump to draw away the hydrogen chloride as fast as it was formed. At the end of about a fortnight hydrogen chloride ceased to come off, and the liquids in the retorts, which had become much thicker and dark coloured, were fractioned.

Under 200° a quantity of unchanged benzyl chloride and phenyl acetate came over, the thermometer then rapidly rising to about 250°, when decomposition began to take place. On continuing this distillation in a nearly perfect vacuum, however, a considerable amount of a beautiful fluorescent liquid was obtained at about 255°.

This oil was then most carefully fractioned under ordinary pressure and most of it finally obtained, boiling at 310—320°.

This substance when pure distils without the least decomposition, has a disagreeable odour, a slightly yellow tint, and exhibits a beautiful blue fluorescence.

On analysis the following figures were obtained:—

	I.	II.	III.	IV.	V.
C	80·81	80·65	80·83	80·58	80·48
H	6·44	6·62	6·38	6·43	6·51
		VI.	Mean.	$\text{C}_{25}\text{H}_{24}\text{O}_3$.	
C		80·59	80·69	80·64	
H		6·46	6·47	6·45	

On treatment with alcohol and potash, this substance readily saponifies with evolution of heat, the saponification being quite complete after heating for half an hour.

On treating the product with water, an oil rose to the surface, which, after washing and drying, was distilled in a vacuum, after which it was found to boil under ordinary pressure between 290° and 300°. This distillate, on being cooled by a freezing mixture, slowly solidified and yielded, after pressing between filter-paper, beautiful white crystals, melting at 39°, and on analysis—

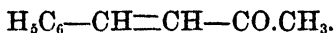
I.	·1246	substance	gave	·3752	CO ₂	·0760	OH ₂
II.	·1676	"		·5050	"	·1023	"
III.	·0606	"		·1829	"	·0371	"
IV.	·1190	"		·3617	"	·0694	"

	I.	II.	III.	IV.	Mean.	C ₁₀ H ₁₀ O.
C....	82·12	82·18	82·31	82·34	82·24	82·19
H....	6·78	6·78	6·80	6·44	6·70	6·85

This substance has an odour somewhat like that of oil of cinnamon and a burning taste. It is almost insoluble in water, but dissolves in most other ordinary solvents, but cannot be crystallised from its solutions. Acetic anhydride and acetyl chloride heated with it effect no change. Chromic acid in glacial acetic acid oxidises it to an uninviting resinous body.

By the action of bromine a very beautiful crystalline bromide is formed, of which, however, we have not yet obtained sufficient to examine.

A possible constitution, the determination of which we reserve for a future occasion, is that of a cinnamyl-methyl ketone—



The alkaline solution from which this oil separated, on being acidulated with sulphuric acid, deposited a quantity of oil which was shaken out with ether and distilled several times in a vacuum.

This oil solidified, on standing for a short time, to a mass of needles very much resembling ordinary phenol. On pressing and drying, they were obtained perfectly white, and of melting point 80° to 81° and boiling at 320° to 322°.

They gave on analysis—

I.	·1458	substance	=	·4513	CO ₂	·0866	OH ₂
II.	·1070	"	=	·3319	"	·0649	"
III.	·1360	"	=	·4194	"	·0810	"

	I.	II.	III.	Mean.	C ₁₃ H ₁₂ O.
C	84·44	84·59	84·10	84·38	84·77
H	6·60	6·74	6·62	6·65	6·52

The substance is slightly soluble in water, forms a sulpho-acid with sulphuric anhydride (Nordhausen sulphuric), and with acetic anhydride an acetate which, when purified by distillation in a vacuum, boils under ordinary pressure at 315—320°.

This acetate has a peculiar odour, is insoluble in water, and very easily saponified by potash.

Its analysis yielded the following numbers:—

I. ·1412 substance gave—

·4111 CO₂
·0810 OH₂.

II. ·1118 substance gave—

·3261 CO₂
·0651 OH₂.

	I.	II.	Theory for C ₁₈ H ₁₁ O(C ₂ H ₅ O).
C	79·40	79·55	79·64
H.....	6·37	6·46	6·19

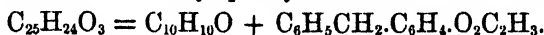
The body (C₁₈H₁₂O), of which this is the acetate, may be represented by the formula C₆H₅.CH₂.C₆H₄.OH, which is that of a benzyl-phenol.

This body was prepared by Paternò (*Ber.*, 5, 288, and 6, 1208), by the direct action of benzyl chloride and zinc-dust on phenol, and from benzanisole with hydriodic acid. He describes it as white needles melting at 84°, slightly soluble in water, and forming an acetate which boils at 317°, and gives a sulphonic acid when warmed with sulphuric acid.

The difference in melting point between our preparation and Paternò's is probably due to a slight impurity in the former. On distilling the residual liquid from which the benzyl-phenol was precipitated by sulphuric acid, an acid distillate was obtained. On neutralising this with silver carbonate, a crystalline silver salt was obtained which gave the following figures on analysis:—

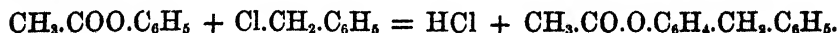
I. ·2829 substance gave ·1829 Ag = 64·67 per cent.
II. ·2322 „ „ ·1502 Ag = 64·68 „
CH₃COOAg = 64·66 per cent.

The original oil, C₂₅H₂₄O₃, contained therefore an acetyl group, and is possibly a mixture of benzyl-phenyl acetate and the body C₁₀H₁₀O.



The difference in boiling point of these two bodies is so slight that it would be almost impossible to separate them by fractional distillation.

The benzyl-phenyl acetate is probably formed as represented by the equation:



The body, C₁₀H₁₀O, is probably produced by a secondary reaction, the equation for which we are not yet in a position to state.

Action of Aluminium Chloride on a Mixture of Benzyl Chloride and Phenyl Acetate.

As the action of benzyl chloride on acetate of phenyl is very slow, it occurred to us that a small quantity of aluminium chloride might accelerate the action.

A mixture of two-thirds of phenyl acetate and one of benzyl chloride was found to work very well in this reaction. On warming in retorts with inverted condenser with small quantities of aluminium chloride, violent action took place, torrents of HCl being evolved; the escaping gas carrying over a light boiling liquid which was condensed by passing the fumes through a tube immersed in a freezing mixture of ice and salt.

The reaction was completed in fifteen to twenty minutes, when the contents of the retort were submitted to fractional distillation, when a distillate was obtained between 100—150°, a small quantity of unacted upon material up to 200°, the thermometer then rising rapidly to 280°, between which temperature and 360°, a considerable fraction was obtained. The distillation was further carried on until decomposition commenced.

The low-boiling fraction was mixed with the portion carried over by the stream of hydrochloric acid, and on being fractioned boiled between 110° and 150°, smelling strongly of acetic anhydride. It was therefore boiled with water, in which part remained insoluble as an oily layer. The aqueous portion was neutralised with silver carbonate and the silver salt recrystallised and submitted to analysis with the following results:—

- I. .2157 substance gave .1394 Ag = 64.63 per cent.
 II. .1978 „ .1274 Ag = 64.51 „
 Theory for CH_3COOAg = 64.66 per cent. Ag.

Acetic anhydride is therefore one of the products of this reaction.

The oily layer which separated, as just alluded to, was dried and fractioned several times over sodium, and obtained finally boiling between 110—112°. It possessed a distinct odour of toluene. The following figures were obtained on analysis:—

- I. .1746 substance gave—
 .5836 CO_2
 .1406 OH_2 .
 II. .1470 substance gave—
 .4920 CO_2
 .1161 OH_2 .

	I.		Theory for C_7H_8 .
C	91.16	91.28	91.30
H	8.94	8.77	8.65

There is, therefore, little doubt that the body is toluene.

The oil boiling between 280° and 360° was found, after repeated fractionation, to boil between 318° and 322°, and was to all appearance

identical with the body $C_{25}H_{24}O_3$, resulting from the action of benzyl chloride alone on phenyl acetate.

On analysis—

I. .1575 substance gave—
·4665 CO_2
·0935 OH_2 .
II. .1416 substance gave—
·4175 CO_2
·0818 OH_2 .

which give the following percentages:—

	I.	II.	Theory for $C_{25}H_{24}O_3$.
C.....	80·77	80·33	80·64
H.....	6·59	6·42	6·45

The substance is therefore identical with that produced by the first action (benzyl chloride and phenyl acetate alone), which was further confirmed by its behaviour on saponification, benzyl-phenol, $C_{10}H_{10}O$, and acetic acid being formed.

The next higher fraction, which was nearly solid, was mixed with a little alcohol, in which the crystals were nearly insoluble, and filtered. After recrystallisation from boiling alcohol, beautiful white crystals with a blue fluorescence were obtained, melting at 213° .

On analysis—

	·0990 substance gave—	
	·3443 CO ₂	
	·0515 OH ₂ .	
		Theory for C ₁₄ H ₁₀ .
C	94·85	94·38
H	5·77	5·62

The body is therefore anthracene.

This reaction affords the easiest method of formation of the body $C_{25}H_{24}O_3$, although the product is somewhat more difficult to purify from the accompanying anthracene.

The products of the reaction with the aid of aluminium chloride are therefore toluene, anthracene, acetic anhydride, and the substance $C_{25}H_{24}O_3$.

As it was possible that the toluene and anthracene might be produced from the benzyl chloride alone, under the influence of the aluminium chloride, we tried heating the two together with the following results:—

Aluminium Chloride on Benzyl Chloride.

On gently heating the two substances, very violent action commences, torrents of HCl being given off, and the liquid becoming black

and thick. On being submitted to fractional distillation, a portion was obtained boiling between 100° and 150° , with a strong odour of toluene, the thermometer rapidly rising to 360° , above which temperature a thick brown oil distils over.

This on cooling deposited a quantity of crystals.

After several distillations over sodium, the fraction $100\text{--}150^{\circ}$ was brought down to $110\text{--}112^{\circ}$. It has a strong odour of toluene, and gave, on combustion, the following figures:—

I. $\cdot 1175$ substance gave—

$\cdot 3961$ CO_2

$\cdot 0947$ OH .

II. $\cdot 1353$ substance gave—

$\cdot 4540$ CO_2

$\cdot 1062$ OH .

	I.	II.	Theory for C_7H_8 .
C....	91.93	91.37	91.39
H....	8.95	8.71	8.70

It was further identified as toluene by conversion into nitrotoluene.

The high-boiling portion, after several distillations, gave a fraction which solidified for the most part.

The solid was purified by pressure between filter-paper and repeated crystallisation from alcohol, when it was obtained beautifully white with the characteristic blue fluorescence of anthracene. It also melted at $212\text{--}213^{\circ}$. For further confirmation it was oxidised to anthraquinone, and the zinc-dust potash reaction obtained.

This reaction explains the formation of toluene and anthracene from the mixture of benzyl chloride and phenyl acetate and aluminium chloride.

It may be observed that the benzyl chloride employed was from Kahlbaum's, and had been several times fractioned to ensure its freedom from toluene.

Weber and Zincke (*Ber.*, 8, 1406) obtained, by the action of water on benzyl chloride, toluene, benzyl-toluene, anthracene, and a quantity of high-boiling hydrocarbons; the products of the reaction corresponding closely with ours, with the exception of benzyl toluene, which we have not succeeded in isolating, although we obtained a large quantity of oils boiling above 360° .

With aluminium chloride and phenyl acetate alone the reaction is very violent, most of the acetate being completely carbonised, and acetic anhydride being the only body obtained in recognisable quantity.

LXVII.--On the Sulphides of Vanadium.

By WILLIAM E. KAY, Dalton Chemical Scholar in the Owens College.

IN his well-known research on vanadium, published in 1831, Berzelius (*Pogg. Ann.*, 22, 1) describes two sulphides:—

(1.) Vanadinsvalighet, VS_2 ,

(2.) Vanadinsvafva, VS_3 ,

the English names for these substances being—(1) Vanadium bisulphide, and (2) Vanadium persulphide.

No addition of importance was made to our knowledge concerning the chemistry of vanadium until Roscoe (*Phil. Trans.*, 1868, 1; 1869, 679; 1870, 317) in 1867—70 published his investigations on the subject, revolutionising our views concerning vanadium and its compounds by proving that the substance hitherto supposed to be the metal is an oxide, and that consequently all the compounds described by Berzelius must also contain oxygen.

Roscoe at the same time found it necessary, from considerations of the chemical relationships of vanadium, to take its atomic weight at one-half that previously assigned to it, and the double correction of Berzelius's formulæ is effected by the substitution in them of the expression V by the one V_2O_3 .

It is, however, a singular fact that whilst this correction has been applied to the other vanadium compounds, the sulphides have in most treatises and dictionaries of chemistry been described as non-oxygenated products, having the formulæ V_2S_4 and V_2S_6 [$=(V_2S_2)_2S_2$ and $(V_2S_2)_3S_2$]. In one or two instances, however, Berzelius's formulæ have been correctly translated into their modern equivalents, $(V_2O_3)_2S_2$ and $(V_2O_3)_3S_2$.

If, on the one hand, these compounds prepared by Berzelius are oxysulphides, it is as well that the fact should be distinctly recognised; whilst, on the other hand, if they are true sulphides, they acquire a special interest as forming the only series of non-oxygenated vanadium compounds obtained by Berzelius, the accurate examination of which could hardly have failed to reveal to him the fundamental error underlying his investigation.

The necessity of a re-examination of these products is therefore evident, and at Dr. Roscoe's request I have carried out an investigation of the whole subject of the compounds formed by vanadium and sulphur, the results of which I have now the honour to lay before the Chemical Society.

Method of Analysis.

Before proceeding to give the experimental details, it will be convenient to describe shortly the method devised for the analysis of these compounds of vanadium and sulphur, especially as the process is equally applicable to the analysis of other sulphides, which, when heated in a stream of air or oxygen, give off all their sulphur as sulphur dioxide, leaving a residue of metallic oxide.

The substance to be analysed is weighed out into a tared porcelain boat, and this is transferred to a hard glass tube contained in an ordinary combustion furnace. The end of the tube nearest which the boat is placed is connected with a gas apparatus supplying pure air or oxygen (preferably the latter), whilst the other end is drawn out and attached to two series of potash-bulbs, the first of which contains strong bromine-water, whilst the second is filled with distilled water.

A slow current of oxygen is allowed to pass through the apparatus, and the tube is heated, first at some little distance behind the boat, the heat being afterwards gradually extended to that part of the tube in which the substance is placed. Any free sulphur which volatilises may be burnt to dioxide by first heating the tube in front and then very gradually extending the heat backwards, when the sulphur is completely burnt in passing through the heated portion of the tube. The sulphur dioxide is swept forward into the bromine-bulbs and there completely oxidised, whilst a residue of pure vanadium pentoxide remains in the boat, and from its weight the amount of vanadium present is readily ascertained.

During the progress of the experiment bromine-vapours are carried forward by the stream of gas and absorbed by the water contained in the second set of bulbs. Not only is the greater part of the bromine-vapour thus kept from passing into the air, but the absorption of every trace of sulphur dioxide is secured by the gas passing through this second series of bromine-bulbs.

In the combustion of the sulphur a small quantity of sulphur trioxide is always formed, and this combined with a trace of water, which is invariably present, remains as sulphuric acid in the combustion-tube. At the conclusion of the experiment the boat containing the pentoxide is removed and weighed. The contents of the bulbs, together with the washings of the combustion-tube, are transferred to a flask and boiled until the excess of bromine is driven off, a small funnel being placed in the neck of the flask to prevent loss by spirting.

A solution is thus obtained containing all the sulphur as sulphuric acid, together with some hydrobromic acid formed during the oxidation.

tion of the sulphur dioxide, and in this the sulphuric acid is determined by precipitation in the usual way.

The following numbers obtained in the combustion of pure sulphur show that the method is a reliable one:—

(a.)	0.2084	substance	gave	1.4820	BaSO ₄ .
(b.)	0.1606	„		1.2314	„
(c.)	0.1766	„		1.2856	„
(a.)	(b.)	(c.)		Mean.	
100.18	99.82	100.06		100.02	per cent. of S.

EXPERIMENTS ON BERZELIUS'S COMPOUNDS.

As has been stated, Berzelius in his paper on the vanadium compounds describes two sulphides—the disulphide, VS_2 , and the persulphide, VS_3 ; and these corrected for his omission of oxygen and for the alteration in the atomic weight of vanadium would now be written $(\text{V}_2\text{O}_2)\text{S}_2$ and $(\text{V}_2\text{O}_2)\text{S}_3$. As, however, these have generally been described as V_2S_4 and V_2S_5 , the question as to what is their true constitution has yet to be decided. Berzelius states that both these compounds may be obtained by precipitation in the wet way, and that one of them, the bisulphide, can also be prepared by a dry process. For a reason, which will be afterwards apparent, these two methods will be treated separately.

(1.) *Berzelius's Persulphide obtained by Precipitation.*

In the preparation of this and the succeeding compound Berzelius's methods have been generally followed, special precautions against oxidation having in addition been adopted. The persulphide was prepared by saturating sodium vanadate with sulphuretted hydrogen and pouring the resulting liquid into an excess of dilute sulphuric or hydrochloric acid diluted with ten volumes of water. The precipitate formed, after washing in the cold with sulphuretted hydrogen water and drying in an atmosphere of carbon dioxide, was found to contain a large quantity of sulphur, a fact not mentioned by Berzelius. This was removed by washing with hot carbon disulphide, the operation being carried out in a funnel surrounded by a water-jacket kept at a temperature of 50° by a current of steam. The top of the funnel was closed by a glass plate, through a circular hole in the centre of which the delivery tube of a stoppered glass globe containing the carbon disulphide passed, and thus by regulating the flow of the liquid the hot disulphide percolated slowly through the substance under treatment. The sulphide thus purified, after drying at 120° in an atmo-

sphere of carbon dioxide until its weight was constant, was found still to retain water of hydration amounting to from 5 to 7 per cent.

For purposes of analysis the vanadium and sulphur were determined by the method already described. The water was estimated by combustion with lead oxide and the oxygen determined by difference.

Of the following preparations No. 1 was obtained by precipitation with sulphuric acid, and Nos. 2 and 3 by precipitation with hydrochloric acid:—

No. 1. 0.2312 substance gave 0.1499 V_2O_5 and 0.7594 $BaSO_4$; 0.4042 substance gave 0.0236 H_2O .

No. 2. 0.2428 substance gave 0.1402 V_2O_5 and 0.8440 $BaSO_4$; 0.3906 substance gave 0.0264 H_2O .

No. 3. 0.2464 substance gave 0.1602 V_2O_5 and 0.7686 $BaSO_4$; 0.4198 substance gave 0.0190 H_2O .

From these numbers the composition of the anhydrous compounds is found to be as follows, the calculated composition of $(V_2O_2)_S_3$ and V_2S_5 being appended for purposes of comparison:—

	No. 1.	No. 2.	No. 3.	Mean.	$(V_2O_2)_S_3$.	V_2S_5 .
V	38.70	34.81	38.25	37.25	44.44	39.04
S.	47.95	51.28	44.91	48.05	41.67	60.96
O	13.35	13.91	16.84	14.70	13.89	—

These numbers show that the product is an oxy-compound, but they do not warrant the assumption of the formula $(V_2O_2)_S_3$. Indeed the variable composition of the precipitate precludes the assignment to it of any definite formula.

(2.) *Berzelius's Bisulphide obtained by Precipitation.*

In the preparation of this compound the pentoxide was dissolved in hydrochloric acid, the excess of acid removed by evaporation, water added, the vanadium reduced by sulphuretted hydrogen, and the precipitated sulphur removed by filtration. Freshly prepared ammonium hydrosulphide was then added in excess and the resulting liquid poured into an excess of dilute sulphuric or hydrochloric acid. The precipitates thus obtained were purified and analysed as described under the foregoing compound.

Of the following preparations Nos. 1 and 2 were prepared by precipitation with sulphuric acid, and Nos. 3 and 4 by precipitation with hydrochloric acid:—

No. 1. 0.2116 substance gave 0.1168 V_2O_5 and 0.8668 $BaSO_4$; 0.2846 substance gave 0.0114 H_2O .

No. 2. 0.2133 substance gave 0.1353 V_2O_5 and 0.7210 $BaSO_4$; 0.3352 substance gave 0.0168 H_2O .

No. 3. 0.2113 substance gave 0.1227 V_2O_5 and 0.8254 $BaSO_4$; 0.3235 substance gave 0.0138 H_2O .

No. 4. 0.2056 substance gave 0.1322 V_2O_5 and 0.6578 $BaSO_4$; 0.2960 substance gave 0.0182 H_2O .

The following numbers give the composition of the anhydrous compounds, the percentage numbers for $(V_2O_5)_2S_2$ and V_2S_4 being added for comparison:—

	No. 1.	No. 2.	No. 3.	No. 4.	Mean.	$(V_2O_5)_2S_2$.	V_2S_4 .
V	32.31	37.53	34.08	38.49	35.60	51.61	44.46
S	58.66	48.93	56.10	46.86	52.64	32.26	55.54
O	9.03	13.54	9.82	14.65	11.76	16.13	—

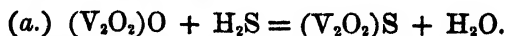
As in the case of the preceding compound, this product is clearly an oxysulphide which does not correspond to the formula generally assigned to it, nor indeed does its variable composition permit of its being represented by any formula whatever.

It may be remarked that in Berzelius's original paper there is no evidence that these products were submitted to analysis, the formulæ assigned to them by him being simply such as he believed them to possess considering the mode of their preparation.

I purpose subjecting these compounds obtained by precipitation to further examination with the object of determining if possible the conditions which govern the variations in the character of the precipitates, and of ascertaining whether they contain or can be converted into any oxysulphide having a simple and definite formula.

(3.) *Berzelius's Bisulphide obtained in the Dry Way.*

With respect to this preparation Berzelius observes:—"When vanadium suboxide [the trioxide] is heated to full redness in sulphuretted hydrogen, it is decomposed by the gas, water and hydrogen are evolved, and the mass finally gains so much in weight as corresponds to 2 atoms of sulphur to 1 atom of metal" (*Pogg. Ann.*, 22, 19). This reaction would be expressed by the following equations, in which (V_2O_5) is the equivalent of Berzelius's metal:—



A careful re-examination of this reaction yielded results as unexpected as they are interesting. A weighed quantity of vanadium pentoxide was reduced at redness in a stream of pure hydrogen, until its weight was constant, and the loss corresponded to a reduction of V_2O_5 to V_2O_3 . This product was then heated in H_2S at redness, and the product from time to time weighed. It required five to six successive

heatings of three hours each before the weight became constant. The gain of weight then corresponded fairly to a conversion of V_2O_3 into $(V_2O_2)S_2$. This calculated gain is 32 per cent.; the experimental numbers in three cases were, 34·9, 34·5, and 35·0. The product thus obtained was, however, on examination found to contain *no oxygen*, giving on analysis the following numbers, which show it to be vanadium trisulphide, V_2S_3 :—

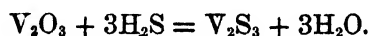
No. 1. 0·2408 substance gave 0·2162 V_2O_5 and 0·8625 $BaSO_4$.

No. 2. 0·2456 " 0·2202 " 0·8776 "

No. 3. 0·2404 " 0·2164 " 0·8498 "

	No. 1.	No. 2.	No. 3.	Mean.	V_2S_3 .
V	50·47	50·37	50·59	50·48	51·62
S	49·26	49·12	48·61	48·99	48·37

The formation of the sulphide is therefore the result of the following simple reaction :—



On comparing this equation with those already given as embodying Berzelius's explanation of the reaction which here takes place, it is apparent that the percentage gain of V_2O_3 in passing into V_2S_3 is identical with that which would ensue on its passage into $(V_2O_2)S_2$, and, moreover, that the percentage amounts of vanadium in the products would be the same in both cases.

The difference between the two substances, however, at once becomes evident when the amount of sulphur present in them is determined, and had Berzelius made a complete analysis of the product, he would have obtained percentage numbers adding up to 116, due to his calculating from the weight of V_2O_3 the weight of his supposed metal (in fact, V_2O_2) present. He would thus have been led into an inquiry which would in all probability have resulted in his ascertaining the true nature of metallic vanadium and of the vanadium compounds.

I shall now proceed to a systematic description of the results I have obtained as to the methods of preparation and properties of the compounds of

VANADIUM AND SULPHUR.

Vanadium forms three sulphides, corresponding with three of the four distinctly characterised oxides of vanadium :—

Sulphides.		Oxides.	
Vanadium disulphide . . .	V_2S_2	Vanadium dioxide . . .	V_2O_2
Vanadium trisulphide . . .	V_2S_3	Vanadium trioxide . .	V_2O_3
—		Vanadium tetroxide . .	V_2O_4
Vanadium pentasulphide .	V_2S_5	Vanadium pentoxide . .	V_2O_5

(1.) *Vanadium Disulphide, V_2S_2 .*

The lowest oxide of vanadium which can be obtained by reduction in hydrogen at redness is the trioxide, V_2O_3 . In the sulphur series, however, the reducing action of hydrogen proceeds further, notwithstanding the fact that sulphuretted hydrogen is a much less stable compound at a red heat than is the vapour of water.

When the trisulphide of vanadium, which will be next described, is heated to intense redness in hydrogen, sulphuretted hydrogen is slowly evolved, and a reduction to disulphide gradually takes place. In carrying out this experiment, which lasts from four to eight days, according to the quantity experimented on, the greatest care has to be taken that the hydrogen is perfectly dry, and is absolutely free from occluded oxygen, as the sulphide is oxidised with the greatest readiness and the results are thus vitiated. In the preparation of this sulphide, all the precautions have to be adopted that were described by Roscoe for the preparation of metallic vanadium. The hydrogen generator is a continuous one, in which, by a supply of dilute sulphuric acid at the top, and a withdrawal of zinc sulphate solution at the bottom of the generator, an uninterrupted stream of hydrogen may be obtained for many days in succession. The gas is purified by passing through wash-bottles, the first containing alkaline lead acetate solution, the second silver nitrate solution, and the three following ones boiled sulphuric acid; the hydrogen then passes through a long horizontal tube containing pumice-stone moistened with boiled sulphuric acid; it is next passed over a column of heated spongy platinum, where any trace of occluded oxygen is converted into water, and this is again absorbed by a second pumice and sulphuric acid tube. All the india-rubber joints are soaked in melted paraffin, and put on hot, then wrapped with copper wire, and finally covered with melted paraffin. At the point where the hydrogen delivery tube is connected with the porcelain tube containing the substance, the junction is surrounded by a jacket filled with melted paraffin. The material is contained in a porcelain or platinum boat, and the porcelain tube carrying this is heated to very intense redness at the full heat of a Hofmann's gas furnace. When the apparatus has to be left over night, a slow stream of hydrogen is allowed to pass continuously through the apparatus, and on re-commencing the experiment, the spongy platinum is heated for some time before the furnace is lighted.

The sulphuretted hydrogen, which is at first evolved with fair rapidity, gradually diminishes in quantity, and at last the amount becomes very small indeed; but in no case have I succeeded in getting rid of the last traces of sulphur, even after 72 hours' heating at the highest temperature of the Hofmann furnace.

The percentage loss, as well as the analytical numbers, whilst agreeing fairly well with the calculated amounts, still show that a small portion of the trisulphide is not completely reduced to disulphide. The calculated percentage loss of sulphur is 16·5; the actual loss of 0·86 gram, after heating for 25 hours, was 15·5 per cent. In the following cases the composition of several preparations of disulphide are given. No. 1 was heated 25 hours; No. 2, 22 hours; No. 3, 40 hours; and No. 4, 72 hours:—

No. 1.	0·2042	substance	gave 0·2116 V ₂ O ₅ and 0·5976 BaSO ₄			
No. 2.	0·2446	„	0·2540	„	0·7244	„
No. 3.	0·2554	„	0·2662	„	0·7416	„
No. 4.	0·2198	„	0·2308	„	0·6437	„
	No. 1.	No. 2.	No. 3.	No. 4.	Mean.	V ₂ S ₃ .
V	58·24	58·34	58·57	59·00	58·54	61·53
S	40·24	40·70	39·93	40·27	40·28	38·46

The disulphide forms glistening black scales, having a slight bronze lustre, or a brownish-black powder, according as it is prepared from the scaly or powdery trisulphide. The specific gravity of the scaly form is 4·2, and that of the powder, 4·4. When heated it unites with oxygen with the greatest avidity. A specimen of the disulphide, which after moistening with water, had been dried at about 130° in carbon dioxide, was taken out into the air whilst hot, and then absorbed oxygen so rapidly, that it became incandescent, and sulphur dioxide was evolved. When heated in the air, sulphur dioxide is given off, whilst the substance passes through the stages of blue and black oxide into the fused crystalline pentoxide. If it be heated in a limited supply of air, free sulphur is also given off, the oxygen being retained by the vanadium.

Boiling hydrochloric acid, both strong and dilute, and boiling dilute sulphuric acid attack the disulphide but very slightly; cold strong sulphuric acid does not act upon it, but it is dissolved by the hot acid to a greenish-yellow solution. Dilute nitric acid attacks the sulphide slowly, the solution being coloured blue; with the hot dilute acid the action is more rapid, whilst by the strong hot acid the substance is violently oxidised, and the solution contains vanadic sulphate.

Caustic soda and ammonia attack the vanadium sulphide but slightly, either in the cold or on heating; yellow ammonium sulphide slowly dissolves the disulphide forming a wine-red solution, whilst in the case of the freshly prepared colourless ammonium hydrosulphide the liquid acquires a splendid purple tint. Potassium hydrosulphide acts slowly on the disulphide, yielding a violet-red solution.

(2.) Vanadium Trisulphide, V_2S_3 .

This is the most important sulphide of vanadium, as it forms the

starting point for the preparation of the other sulphides. It also possesses a special interest as being the only pure non-oxygenated vanadium compound obtained by Berzelius, in his investigation of this metal and its compound.

Vanadium trisulphide is produced in the following methods:—

(1.) By the action of sulphuretted hydrogen on the trioxide at redness. This reaction was described by Berzelius, and has already been fully considered (*see* p. 732).

It is, however, not necessary to prepare the trioxide for this purpose, as sulphuretted hydrogen acts similarly on the pentoxide. The first action is a reduction of the pentoxide to trioxide, this being evident from the fact that the pentoxide first loses, and afterwards gains in weight.

That the product is the trisulphide will be seen from the following analysis of a preparation obtained by heating the pentoxide to full redness in sulphuretted hydrogen for 13 hours.

0·2265 gram gave 0·2073 V_2O_5 , and 0·7870 $BaSO_4$.

		V_2S_5 .
V.....	51·42	51·62
S.....	47·77	48·37

(2.) Vanadium trisulphide is also formed by the action of sulphuretted hydrogen at redness on any chloride of vanadium, or on vanadyl trichloride, $VOCl_3$. It was by this reaction that I first obtained a true sulphide of vanadium, for after convincing myself that Berzelius's precipitation products were oxy-compounds, I sought for a new method of preparing the sulphides. This mode of production by means of the chlorides is not, however, suitable for the preparation of the sulphide in quantity, as the chlorides of vanadium are prepared only with considerable difficulty. Sulphuretted hydrogen attacks the liquid tetrachloride in the cold; the substance becomes very hot, and the trichloride is formed with separation of sulphur and evolution of hydrochloric acid:—



The dichloride and trichloride of vanadium are not attacked until a temperature approaching redness is attained. At full redness the action proceeds rapidly, hydrochloric acid is evolved, and the trisulphide is formed, irrespective of the special chloride which is subjected to the reaction.

This is seen from the following analytical data:—

No. 1.	0·2048 gram gave	0·1794 V_2O_5	and	0·7235 $BaSO_4$
No. 2.	0·1980	„	0·1706	„ 0·6997 „
No. 3.	0·2041	„	0·1812	„ 0·7275 „
No. 4.	0·2060	„	0·1832	„ 0·7340 „
No. 5.	0·2101	„	0·1868	„ 0·7560 „

	No. 1. From VCl ₃ .	No. 2. From amor- phous VCl ₃ .	No. 3. From scaly VCl ₃ .	No. 4. From VCl ₄ .	No. 5. From VOCl ₃ .	V ₂ S ₃ .
V . . .	49·23	48·41	49·90	49·98	49·97	51·62
S	48·57	48·59	49·02	48·99	49·48	48·37

(3.) Vanadium trisulphide is directly produced from the pentoxide by the action of carbon disulphide vapour at redness. This method I have found to be the most convenient for the preparation of the trisulphide in quantity. The operation is conducted as follows. A slow current of pure dry carbon dioxide is passed through carbon disulphide contained in a flask heated in a water-bath, the temperature of which is maintained by a jet of steam. The carbon dioxide charged with the disulphide vapour then passes over the pentoxide, contained in a hard glass tube, placed in a combustion furnace. The posterior end of the combustion-tube is drawn out and connected with a condenser for the recovery of the excess of carbon disulphide. The air in the apparatus is first displaced by carbon dioxide, and the pentoxide in the furnace is then heated to redness, whilst the temperature of the water-bath is raised to 50° and maintained at this temperature, the current of carbon dioxide being allowed to pass but slowly. In this way a slow passage of carbon disulphide vapour is obtained through the apparatus, and a steady condensation of carbon disulphide takes place at the posterior end. The reaction commences readily, and large quantities of sulphur are deposited and sulphur dioxide evolved. Carbon dioxide is no doubt also formed in the reaction, but the conditions of the experiment do not permit of the direct observation of this fact. By this method 20 grams of pentoxide may be converted into sulphide in from six to ten hours. The condensed carbon disulphide after rectification over lime may be again used for the preparation of the trisulphide.

The following numbers were obtained in analyses of four preparations thus obtained:—

- No. 1. (a.) 0·1999 substance gave 0·1816 V₂O₅, and 0·6977 BaSO₄.
 (b.) 0·1999 „ 0·1810 „ ; 0·2024 substance
 gave 0·7062 BaSO₄.
 No. 2. 0·2731 substance gave 0·2472 V₂O₅; 0·2001 substance gave
 0·6934 BaSO₄.
 No. 3. 0·1678 substance gave 0·1518 V₂O₅, and 0·5828 BaSO₄.
 No. 4. 0·2173 „ 0·1977 „ 0·7569 „

	No. 1.		No. 2.	No. 3.	No. 4.	Mean.	V ₂ S ₃ .
	(a.)	(b.)					
V	51·04	50·88	50·87	50·83	51·13	50·95	51·62
S	47·97	47·97	47·64	47·75	47·88	47·84	48·37

Vanadium trisulphide forms either glistening black scales with graphitic lustre, or a grey-black amorphous powder, according as it is prepared from the scaly chlorides on the one hand or from the oxide on the other. The specific gravity of the scaly product is 3.7, and that of the amorphous powder 4.0. Heated in air or oxygen the trisulphide is oxidised similarly to the disulphide, but much less readily. Sulphur dioxide is evolved, and the blue and black oxides formed, these gradually passing into the pentoxide.

The trisulphide is but slightly attacked by dilute or strong hydrochloric acid, either in the cold or on heating. Hot dilute sulphuric acid also acts upon it but slowly, but by the strong and hot acid it is more rapidly dissolved. Dilute nitric acid acts upon the trisulphide slowly in the cold, and more rapidly on heating, forming a blue solution, as in the case of the disulphide; by the strong acid it is readily oxidised in the cold, whilst in the case of the hot acid the oxidation proceeds with violence.

Caustic soda and ammonia have a slight solvent action on the trisulphide. Yellow ammonium sulphide acts upon the substance slowly, forming a wine-red liquid; whilst with the colourless ammonium hydrosulphide a splendid purple-coloured solution is obtained, identical in appearance with that formed in the case of the disulphide. The colour of the liquid produced on solution in potassium hydrosulphide is violet-red.

Vanadium Pentasulphide, V_2S_5 .

At a temperature of about 400° , vanadium trisulphide takes up two additional atoms of sulphur, forming the pentasulphide, V_2S_5 . For the preparation of this compound the trisulphide is mixed with one-third its weight of sulphur (purified by carbon disulphide), the mixture very finely powdered and placed in a strong narrow tube. The tube, after filling with dry carbon dioxide, is temporarily closed by a cork provided with a narrow capillary tube (to prevent access of oxygen), and the tube is then sealed off as near as possible to the surface of the mixture. The sealed tube is next heated in a hot-air oven for three hours, to a temperature of about 400° (cadmium iodide melting at 404° being used as an indicator). The product, after washing with hot carbon disulphide to remove any free sulphur present, leaves a residue of the pure pentasulphide.

It is inadvisable to use a large excess of sulphur in the preparation of this sulphide, for although the pentasulphide is produced, it retains from 1 to 2 per cent. of sulphur very tenaciously, and the removal of this is a matter of considerable difficulty.

The following table gives the composition of specimens of pentasulphide prepared as before described :—

No. 1. 0·1709 substance gave 0·1139 V_2O_5 and 0·7526 $BaSO_4$.
 No. 2. 0·1770 " 0·1180 " 0·7908 "
 No. 3. 0·1755 " 0·1220 V_2O_5 ; and 0·1740 substance
 gave 0·7507 $BaSO_4$.

	No. 1.	No. 2.	No. 3.	Mean.	V_2S_5 .
V.....	37·46	37·46	39·07	38·00	39·04
S.....	60·56	61·42	59·33	60·44	60·96

Vanadium pentasulphide forms a black powder, having a specific gravity of 3·0. Heated in the air it gives off sulphur dioxide, and is converted into the black oxide, which on further heating passes into the fused pentoxide. If, however, the heat be very carefully applied, some free sulphur is first given off without this taking fire. Heated in a neutral atmosphere, the pentasulphide loses two atoms of sulphur, being converted into trisulphide.

The pentasulphide is but slightly attacked by hot strong hydrochloric acid, and by hot dilute sulphuric acid, whilst by strong sulphuric acid it is slowly dissolved, forming a yellow solution. Hot dilute nitric acid dissolves the pentasulphide slowly, but completely; whilst by the strong acid it is more energetically oxidised.

Ammonia does not easily attack the pentasulphide, but it is readily dissolved by caustic soda, especially on heating, forming a yellow solution. In this respect it differs markedly from the other vanadium sulphides which dissolve but slightly in caustic soda. The pentasulphide is slowly acted upon by the alkaline sulphides. With colourless ammonium hydrosulphide the solution has the splendid purple colour also yielded by the other vanadium sulphides. To obtain this colour in perfection, it is necessary that the hydrosulphide solution shall be completely saturated with sulphuretted hydrogen, and the colour is best obtained by passing sulphuretted hydrogen to excess through ammonia solution containing the pentasulphide in suspension. If the sulphuretted hydrogen be not present in excess, the liquid has a rich carmine-red colour. The solution of pentasulphide in yellow ammonium sulphide is a brownish-red, whilst that in potassium hydrosulphide is wine-red.

Summary.

The foregoing experiments show :—

(1.) That the precipitation products obtained by Berzelius are oxy-compounds, not corresponding either with the formulæ V_2S_4 and V_2S_5 , or with those $V_2O_2S_2$ and $V_2O_3S_3$.

(2.) That the substance obtained by him in the dry way is a true sulphide of vanadium, being the trisulphide, V_2S_3 .

(3.) That, in addition to the trisulphide, two other vanadium sulphides exist, namely, the disulphide, V_2S_2 , and the pentasulphide, V_2S_5 .

(4.) That compared with the oxides, the sulphides of vanadium are compounds of inferior stability; for whilst in the oxygen series the penta-compound is stable at redness in a neutral atmosphere, in the sulphur series the penta- is converted into the tri-sulphide. Again, in hydrogen at intense redness, the trioxide is permanent; whilst the tri-sulphide is under similar conditions reduced to disulphide.

LXVIII.—*On the Action of Organo-zinc Compounds upon Nitriles and their Analogues.* (Second Notice.)

By E. FRANKLAND, F.R.S., and C. COLBORNE GRAHAM, A.I.C.

4. *Action of Zinc-ethyl on Cyanogen.*

AN eight-ounce boiling-flask was inverted over mercury, and a bent glass tube, connected by means of caoutchouc tubing with a Bunsen's pump, was passed up through the mercury so as almost to touch the bottom of the inverted flask. The caoutchouc tubing could be closed by a clip. By means of the Bunsen pump, which was kept in action during the experiment, the mercury was raised almost to the top of the tube, and the clip was then closed. Carbonic anhydride was passed into the flask so as to half fill it, after which 25 grams of zinc-ethyl were introduced. The carbonic anhydride having been drawn off by the pump, cyanogen gas, generated from mercuric cyanide, was passed in, when rapid absorption took place, accompanied by a rise of temperature. The absorption slackened from time to time, owing to the accumulation of a quantity of an indifferent gas, principally ethylic hydride, the formation of which is due to a trace of hydrocyanic acid in the cyanogen. As soon as this gas began to fill the flask the clip was opened, by which means the gas was instantaneously removed, and the absorption proceeded as at first. A strong empty bottle, which acted as a vacuum chamber, was interposed between the clip and the pump. Care was taken to avoid a too great rise of temperature. As the reaction proceeded, the contents of the flask became pasty and of a reddish-brown colour, and by the time the absorption had ceased, the zinc-ethyl had been converted into a solid mass. It was impossible to get rid of the last trace of zinc-

ethyl, as the solid substance enclosed it, and prevented it from being acted upon.

The flask was then removed from the mercury, and having been attached to a condenser, was heated in an oil-bath to 120° . About 4 c.c. of a colourless liquid containing a trace of zinc-ethyl were obtained. The zinc-ethyl was got rid of by connecting the flask containing the liquid with a gas holder of oxygen, and agitating the liquid with this gas as long as any absorption took place, the flask being kept cool by immersion in ice and water. The liquid was then redistilled, and it boiled steadily at 96° . The following results were obtained by combustion:—

0.1949 gram gave 0.4685 gram carbonic anhydride and 0.1624 gram water.

	Calculated for C_3H_5N .		Found.
C_3	36	65.45	65.57
H_5	5	9.09	9.26
N	14	25.46	—
	55	100.00	

The substance had thus, as regards carbon and hydrogen, the percentage composition of propionitrile, and to this compound its boiling point, odour, and other properties also pointed. No odour of the normal cyanide could be perceived.

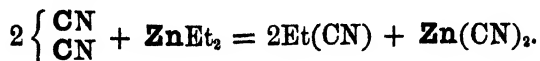
As a further proof, a portion of the liquid was saponified with alcoholic potash, and the potassic propionate thus obtained was distilled with dilute sulphuric acid. The distillate of dilute propionic acid was converted into the barium salt, of which a barium determination gave the following result:—

0.4015 gram barium salt dried at 130 — 140° gave 0.3292 gram baric sulphate, corresponding to 0.1936 gram barium.

	Calculated for $C_6H_{10}O_4Ba$.	Found.
Barium in 100 parts	48.41	48.22

The solid residue remaining after the removal of the propionitrile consisted almost entirely of zincic cyanide. On the addition of water it evolved very little gas, showing the absence of zinc-monethyl compounds. Boiling alcohol extracted from it a small quantity of a brownish oil. The solid matter remaining after treatment with alcohol dissolved completely in hydrochloric acid, evolving a strong

odour of hydrocyanic acid. The action of zinc-ethyl on cyanogen may therefore be expressed by the equation—



It is noteworthy in this reaction that a separation of carbon from carbon accompanied by a simultaneous union of carbon to carbon occurs, both processes taking place at ordinary temperatures. In other respects the action is strictly analogous to that discovered by Gal (*Annalen*, 147, 126), in which by the action of cyanic chloride on zinc-ethyl, propionitrile and zincic chloride were obtained.

LXIX.—*Action of Zinc-ethyl on Benzoylic Cyanide.*

By E. FRANKLAND, F.R.S., and D. A. LOUIS, Esq.

THE benzoylic cyanide employed in the following experiments was prepared in the usual manner by distilling benzoylic chloride with mercuric cyanide. The distillate solidified in large crystals, from which a small quantity of liquid could be poured off. After rectification of the crystals, the compound was obtained in a state of purity.

Zinc-ethyl was diluted with about three times its volume of dry ether, and to this solution benzoylic cyanide was added in small portions. It was not necessary to pulverise the cyanide, as the heat of the reaction caused it at once to liquefy and dissolve. The action, which is somewhat violent, was in each case allowed to subside before the addition of fresh cyanide. If the temperature rose to the boiling point of the ether, the flask was immersed in cold water. The colour of the liquid gradually changed to a light reddish-brown. As soon as the action became sluggish a wide upright tube was fitted to the flask, which was then heated on a water-bath. In this way the ether was gradually expelled, and the reaction was completed. The heating was continued until the evolution of gas, which had gone on during the whole of the experiment, ceased. This gas was not examined.

The product of the reaction, an amber-coloured jelly, was now decomposed by the addition of an excess of alcohol. Very little gas was evolved in this process, both semi-molecules of ethyl in the zinc-ethyl molecule having apparently been used up in the reaction. When the decomposition was complete, the contents of the flask were digested

with boiling alcohol, and the liquid filtered hot from the zincic hydrate. The filtrate deposited on cooling large tufts of colourless needles. By again exhausting the zinc hydrate with boiling alcohol, a second, but smaller crop of these crystals was obtained. This body, which was evidently perfectly homogeneous, was recrystallised once from boiling alcohol. It fused at $123-124^{\circ}$, and its fusing point was not altered by further recrystallisation. It was nitrogenous, and did not contain zinc. Analysis yielded the following results:—

- I. 0.1667 gram gave 0.4957 gram carbonic anhydride and 0.0836 gram water.
- II. 0.2089 gram gave 0.6227 gram carbonic anhydride and 0.1045 gram water.
- III. 0.0910 gram burnt with copper oxide in a vacuum gave a volume of nitrogen corresponding to 0.0036404 gram.
- IV. 0.0900 gram gave a volume of nitrogen corresponding to 0.0036647 gram.

These numbers agree with the formula $C_{24}H_{19}NO_2$.

	Calculated.		Found.				
			I.	II.	III.	IV.	Mean.
C_{24}	288	81.58	81.11	81.29	—	—	81.20
H_{19}	19	5.38	5.57	5.55	—	—	5.56
N	14	3.97	—	—	4.00	4.07	4.03
O_2	32	9.07	—	—	—	—	(9.21)
	<hr/>	<hr/>					
	353	100.00					100.00

We propose to name this substance *benzcyanidin*, but we are unable at present to suggest a constitutional formula for it, or even an equation for its formation. The yield is but small, amounting to not more than 3 per cent. of the benzoyle cyanide. The only reaction which we have as yet tried with it is the action of concentrated hydrochloric acid at 150° . Among the products of decomposition we were able to identify benzoic acid and ammonia.

The filtrate from the white crystals was distilled. After the alcohol had passed over, the thermometer rose quickly to 200° , and between this temperature and 220° a considerable fraction was obtained. The temperature then rose to about 250° , at which point the distillate solidified in the receiver, and was found to consist of benzoic acid. Above this temperature the small quantity of substance still remaining in the retort began to decompose, and was not further examined.

The fraction boiling between 200° and 220° possessed the characteristic odour of the fatty-aromatic ketones. On attempting to purify it by repeated distillation, it was found that no fraction of a fixed boil-

ing point could be obtained. The liquid contained nitrogen, and as we suspected that this was due to the presence of a small quantity of unaltered benzoic cyanide, which from its boiling point ($206-208^{\circ}$) could not be got rid of by distillation, the entire liquid was boiled with alcoholic potash as long as ammonia was evolved. After distilling off the alcohol and adding water, the oil rose to the surface, and was extracted with ether. The ethereal solution was dried over fused potassic carbonate, and the ether was distilled off, when the liquid boiling between 200° and 220° was recovered, apparently but little diminished in quantity. It was now free from nitrogen, but as regards constancy of boiling point it had undergone no improvement. Moreover, the various fractions gave varying analytical results. Each time the liquid was distilled it underwent a slight decomposition, water splitting off. As no concordant results could be obtained, it was resolved to oxidise the liquid, and it was accordingly boiled with a mixture of potassic dichromate and dilute sulphuric acid, the oxidising mixture being added in small portions as long as rapid reduction to a chromic salt took place. As soon as this reduction ceased the process was interrupted, and the oil which floated on the surface was separated, treated with sodic carbonate, and dried. It now distilled at 212° , and possessed a pure odour of a fatty-aromatic ketone. The following numbers were obtained by combustion:—

0.1521 gram gave 0.4473 gram carbonic anhydride and 0.1077 gram water.

These results lead to the formula of propiophenone, $C_9H_{10}O$.

	Calculated.		Found.
C_9	108	80.60	80.20
H_{10}	10	7.46	7.90
O	16	11.94	(11.90)
	134	100.00	100.00

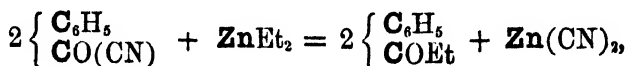
Propiophenone boils at 210° (Popoff).

Both acetic and benzoic acids, the products of the oxidation of propiophenone, were formed in the above process. The acetic acid was identified by a silver determination of its silver salt, the benzoic acid by its melting point.

The propiophenone must either have already been present before oxidation in the liquid boiling between 200° and 220° , or it must have been formed by the oxidation either of ethylphenylcarbinol or of diethylphenylcarbinol. The formation of ethylphenylcarbinol by the action of zinc-ethyl on benzoic cyanide would be difficult to explain. Diethylphenylcarbinol might, however, be formed, the reaction in this

case corresponding to that discovered by Butlerow, in which trimethylcarbinol is obtained by the action of zinc methyl upon acetylic chloride, the chlorine being in the present reaction replaced by cyanogen. As, however, in the reaction discovered by Freund (*Annalen*, 118, 20) for the preparation of propiophenone by the action of zinc-ethyl on benzoyle chloride, no formation of a tertiary alcohol was observed, we think it unlikely that this should take place in the present case.

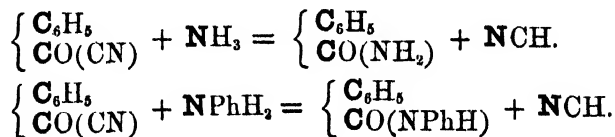
We therefore incline towards the view that the propiophenone was formed directly by the action of zinc-ethyl on the benzoyle cyanide, according to the equation—



the reaction being the exact counterpart of that described by Freund. The insoluble white residue left behind after extracting with alcohol contained a large quantity of zinc cyanide, giving off a strong odour of hydrocyanic acid when treated with hydrochloric acid.

In this and in the preceding paper the halogen nature of the compound radical cyanogen has been shown to extend to its replacement by an electropositive hydrocarbon radical.

We may mention that in order to prove more completely the great similarity between benzoyle cyanide and benzoyle chloride, we tried the action of ammonia and aniline on the former compound, and obtained respectively benzamide and benzanilide—

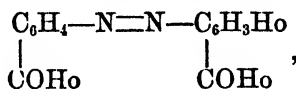


The fusing point of benzanilide, which is not given in Gerhardt's original paper, was found by us to be 159°.

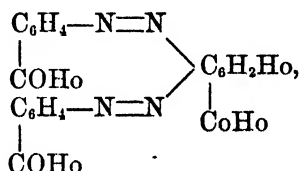
LXX.—On the Action of Diazonaphthalene upon Salicylic Acid.

By PERCY F. FRANKLAND, Ph.D.

ALTHOUGH numerous azo-bodies have been prepared of late years, many even upon a manufacturing scale, yet only few thereof are compounds of the hydroxybenzoic acids; these are hydroxybenzoëdiazobenzoic acid,



and oxybenzoëbidiazobenzoic acid,



prepared by Griess (*Journ. f. Prakt. Chem.* [2], 1, 106) at first by the decomposition of diazobenzoic acid, and later (*Ber.*, 1876, 629) also directly from hydroxybenzoic acid and diazobenzoic acid. Griess has further prepared a parazosulfoxybenzeneazosalicylic acid (*Ber.*, 1880, 716) from paradiazosulfobenzoic acid and salicylic acid, possessing the formula—



Finally, azobenzeneoxybenzoic acid has quite recently been prepared by Stebbins (*Ber.*, 13, 716), by acting with diazobenzene upon salicylic acid.

As yet the above compounds have been but little examined, and in none of them has the position of the phenylazo-group been ascertained.

At the suggestion of Professor Wislicenus, I undertook the following work, the object of which was, besides the preparation of a new azo-compound, the determination of the place of entry of the diazo-group into the benzene nucleus of salicylic acid. The diazo-group was introduced in the form of diazonaphthalene, naphthylazosalicylic acid being formed. The naphthylazosalicylic acid, on treatment with tin and hydrochloric acid, yielded naphthylamine and amidosalicylic acid; the latter was then converted, by means of its diazo-compound, into iodosalicylic acid, which, by its melting point and characteristic reactions, was identified as the iodosalicylic acid already known. To render the proof of its identity still more positive, the iodosalicylic

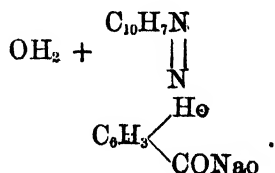
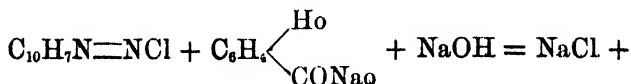
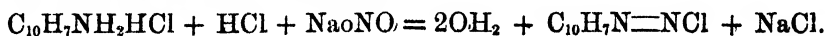
acid was further converted into hydroxysalicylic acid, which proved to be the quinolcarboxylic acid.

Bye-products of some interest were formed in the action of diazonaphthalene upon salicylic acid, which will be referred to below.

Naphthylazosalicylic Acid.

The following numbers show the proportions in which the ingredients were used for its preparation:—

8.98 grams of naphthylamine hydrochloride were dissolved in 500 grams of water, to which was added 1.85 gram of hydrochloric acid; this solution, after filtration, was cooled by immersion in ice, and then treated with 3.45 grams of sodic nitrite dissolved in a little water. The solution assumed a dark-brown colour, and a small quantity of a reddish-brown powder was precipitated; the latter was filtered off as quickly as possible, and the clear solution of diazonaphthalene was run into 6.9 grams of salicylic acid and 6 grams of sodic hydrate dissolved in 500 grams of water. The liquid became orange-coloured, a considerable evolution of nitrogen took place, and a dark-brown precipitate was formed. The mixture was then heated upon the water-bath and filtered hot. The brown residue was several times extracted with boiling water, its further treatment being referred to later under the title of the "brown product." The clear yellow filtrate contains the sodium salt of naphthylazosalicylic acid, which is formed according to the equations:—



Common salt was then added to the solution, causing the dissolved sodium salt of the naphthylazosalicylic acid to separate out as a light-yellow bulky precipitate, which was then filtered off. On acidulating the filtrate with dilute hydrochloric acid, a white precipitate was formed, which was identified as salicylic acid, and its appearance in a quantity equal to about half of that employed shows that the reaction between diazonaphthalene and salicylic acid is only a very partial one, and hence but a small yield of naphthylazosalicylic acid was obtained.

The sodium salt of the naphthylazosalicylic acid was then crys-

tallised from boiling water, and, on analysis, yielded the following numbers:—

Calculated for $C_{10}H_7N_2.C_6H_3<\overset{Ho}{\text{CONaO}}$.

	Theory.	Found.	
N.....	8.92 per cent.	9.25	9.75
Na	7.32 „	7.17	

This sodium salt is nearly insoluble in water (1 part requiring 1,420 parts of cold and 644 parts of hot water). The solution dyes silk a light-yellow colour. Hydrochloric acid precipitates from its aqueous solution free naphthylazosalicylic acid as a grey gelatinous mass, which can be crystallised from boiling benzene. On analysis it yielded the following results:—

Calculated for $C_{10}H_7N_2.C_6H_3<\overset{Ho}{\text{COHo}}$.

	Theory.	Found.		
C	69.86 per cent.	69.52	68.91	69.50
H	4.11 „	4.57	4.37	4.48
N	9.59	—	9.45	—

Decomposition of Naphthylazosalicylic Acid by Tin and Hydrochloric Acid.

The sodium salt was gradually introduced into a mixture of granulated tin and concentrated hydrochloric acid, the mixture being finally heated on the water-bath until all had passed into solution. The products of this reduction are naphthylamine and amidosalicylic acid. The solution containing the tin double salts was first freed from tin by precipitation with sulphuretted hydrogen, and then, after filtration, evaporated down in a stream of carbonic anhydride. The concentrated solution was then rendered alkaline with sodic carbonate, and the precipitated naphthylamine filtered off, the remainder of the naphthylamine being removed by shaking out with ether. The solution (now only containing amidosalicylic acid) was then again rendered acid and evaporated further until the amidosalicylic acid, or rather its hydrochloric acid compound, crystallised out in fine brownish needles.

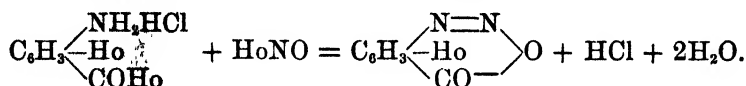
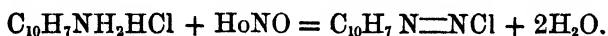
The naphthylamine obtained possessed the correct melting point, and a chlorine determination was made with its hydrochloric acid salt:—

Calculated for $C_{10}H_7NH_2.HCl$.

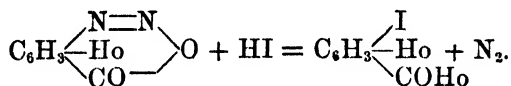
	Theory.	Found.
Cl	19.77 per cent.	19.94

Conversion of the Amidosalicylic Acid into Diazo- and Iodo-salicylic Acids.

The solution containing the hydrochloric acid compounds of naphthylamine and amidosalicylic acid was evaporated down to crystallisation in a stream of carbonic anhydride, and the crystals were stirred up with a small quantity of water, and a stream of nitrous anhydride was then passed through the mixture, which was cooled by immersion in ice. By this means the naphthylamine was converted into diazonaphthalene, which, being very soluble in water, remained in solution; whereas the amidosalicylic acid was transformed into insoluble diazo-salicylic acid, which separated out as a yellow flocculent precipitate—



The precipitated diazosalicylic acid was filtered off and treated with a concentrated solution of hydriodic acid; a violent reaction, accompanied by abundant evolution of nitrogen, took place. The mixture was finally heated for half-an-hour on the water-bath. When cool, it was filtered; the precipitate remaining on the filter was iodosalicylic acid—



After being washed free from excess of hydriodic acid, the residue was dissolved in ammonia, reprecipitated with hydrochloric acid, and then repeatedly crystallised out of boiling water. The melting point of the colourless acid so obtained was 193.5° ; this is 2.5° lower than that given by Goldberg (*Dissertation*, Wurzburg, 1878) as the melting point of paraiodosalicylic acid; but in all other respects the above acid agrees with his. Moreover, I prepared, for the sake of comparison, some paraiodosalicylic acid according to his directions, viz., from paranitrosalicylic acid by means of the amido- and diazo-compounds, and also obtained for it the melting point 193.5° . The iodosalicylic acid gave with a solution of ferric chloride the characteristic violet coloration. There can be no doubt that paraiodosalicylic acid and the iodosalicylic acid obtained from naphthylazosalicylic acid are identical. Analysis gave:—

Theory.	Found.
I = 48.11 per cent.	<div style="display: flex; justify-content: space-around; align-items: center;"> 47.76 47.77 </div>

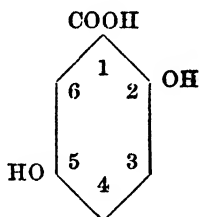
Conversion of the Iodosalicylic Acid into Hydroxysalicylic Acid.

The iodosalicylic acid was fused with an excess of caustic potash, the temperature being maintained at 200°. The fused mass was then dissolved in water, acidulated with hydrochloric acid, and then repeatedly shaken out with ether. On evaporating the ether, dark-coloured needles in rosette-like groups were left behind. The hydroxysalicylic acid so obtained, after purification by recrystallisation, gave on analysis :—

Calculated for $C_6H_5 \begin{matrix} \text{Ho} \\ \text{Ho} \\ \text{COHo} \end{matrix}$.		
	Theory.	Found.
C.	54.54 per cent.	55.18
H	3.90 „	4.26

The melting point was 195—197°. Ferric chloride gave with the acid a deep-blue coloration, becoming dirty-red on addition of sodic carbonate. On dry distillation at 215° it yielded hydroquinone.

From the above evidence, the hydroxysalicylic acid obtained is proved to be identical with parahydroxysalicylic acid, and as the latter possesses the formula



it is thus shown that the diazo-group of the diazonaphthalene attached itself to the benzene-ring of the salicylic acid, just as in the case of most other substitutions suffered by the latter, in the para-position to the hydroxyl, and in the meta-position to the oxatyl.

Examination of the "Brown Product."

It has already been mentioned that in the preparation of naphthylazosalicylic acid, an amorphous brown body insoluble in water is simultaneously formed. It was found that the salicylic acid takes no part in the formation of the latter, but that the same body may also be obtained by simply neutralising a solution of chloride of diazonaphthalene with sodic carbonate.

The brown product consists of a mixture of two bodies; one of which is insoluble in caustic alkalis, whilst the other, which is formed in far smaller quantity, dissolves in sodic hydrate to a deep-crimson solution, from which it is precipitated even by carbonic acid. These two bodies are extremely difficult to obtain in a pure state, but the

one insoluble in alkalis can be got in a minutely crystalline form by precipitating with alcohol from a benzene solution. Both these bodies dissolve in alcohol, ether, benzene, and glacial acetic acid to dark crimson-coloured solutions. The brown body, soluble in alkalis, gave on analysis numbers pointing to the formula $C_{10}H_8NO$:—

	Theory.	Found.
C.	75.95 per cent.	74.79
H	5.06 „	4.88
N	8.86 „	8.46

On the other hand, the brown body insoluble in alkalis gave, on analysis, results corresponding with the formula $C_{50}H_{38}N_6O_2$:—

	Theory.	Found.
C.	81.63 per cent.	81.58
H	4.49 „	4.91
N	9.52 „	9.51

The oxygen does not appear to be combined in the form of hydroxyl, as all attempts to obtain a sodium compound failed.

In order to throw light upon the constitution of these brown bodies, a comparative experiment was made with diazobenzene; but, as will be seen below, the reactions in the two cases are not quite analogous. An aqueous solution of chloride of diazobenzene, on being almost neutralised with sodic hydrate, gave rise to a light-brown precipitation. On extracting the precipitate with boiling sodic hydrate, it was found to consist of two bodies; the one soluble, and the other insoluble in caustic alkalis. Both were obtained in a minutely crystalline state by allowing their saturated boiling alcoholic solutions to cool.

For the body insoluble in alkalis numbers were found, on analysis, agreeing not very closely with any formula, $C_{30}H_{23}N_6O$ being, however, the nearest :—

	Theory.	Found.
C.	76.76 per cent.	75.90
H	4.90 „	4.91
N	14.93 „	14.58

For the light-brown body soluble in alkalis, analysis gave numbers corresponding with the formula $C_{18}H_{14}N_4O$:—

	Theory.	Found.	
C	71.52 per cent.	71.19	71.04
H	4.64 „	5.10	4.92
N	18.54 „	18.62	18.73

For the formula $C_{18}H_{14}N_4O$, there are two principal isomerides, viz. :—



and—



In order to ascertain which of these formulæ belonged to the body in question, the latter was submitted to the reducing action of tin and hydrochloric acid. The only products of decomposition obtained were aniline and a phenol, which was identified as the diamidophenol described by Hemilian (*Ber.*, 8, 768), and these are precisely the products that should be formed if the second formula be the correct one. A body possessing this formula was prepared many years since by Griess (*Jahresb.*, 1864, 435; *Ber.*, 9, 627) under the name of phenol-bidiazobenzene; firstly, by the treatment of nitrate of diazobenzene with barium carbonate, and later by the action of diazobenzene upon phenylazophenol.

Naphthylazo-(α)-naphthol.

The portion of the "brown product," soluble in alkalis, formed in the preparation of naphthylazosalicyclic acid, was at first thought to be naphthylazo-(α)-naphthol, and some of this new azo-compound was therefore prepared in order to compare with the brown body above-mentioned. Naphthylazo-(α)-naphthol is obtained by introducing a solution of chloride of diazonaphthalene into a sodic hydrate solution of α-naphthol; the mixture assumes a deep crimson colour, and on acidulating with hydrochloric acid, the naphthylazo-(α)-naphthol falls out as a dark crimson powder.

The following numbers were obtained on analysis:—

Calculated for $\text{C}_{10}\text{H}_7\text{N}=\text{NC}_{10}\text{H}_7\text{Ho}$.

	Theory.	Found.	
C	80.53 per cent.	80.85	80.42
H	4.69 ,,	4.57	4.47
N	9.39 ,,	8.75	8.70

In conclusion, I wish to express my sincerest thanks to Professor Wislicenus for his kind assistance and invaluable advice in the carrying out of this investigation.

LXXI.—*Acetylorthoamidobenzoic Acid.*

By P. P. BEDSON, D.Sc. (Lond.), Assistant Lecturer and Demonstrator in Chemistry in the Owens College, and A. J. KING, B.Sc.

HOFMANN has shown (*Ber.*, 9, 1302) that acetylparamidobenzoic acid is formed when acetylparatoluidine is oxidised by potassium permanganate. Later, Michael (*Ber.*, 10, 576) obtained in a similar manner

oxysuccinyl- and oxyphthalyl-paramidobenzoic acids from paratolylsuccinamide and paratolyl-phthalimide. These derivatives of paramidobenzoic acid yield the hydrochloride of this acid when boiled with concentrated hydrochloric acid, thus affording a method of preparing paramidobenzoic acid from paratoluidine. The last-mentioned author states that the attempts made to prepare the succinyl and phthalyl derivatives of ortho-amidobenzoic acid were unsuccessful. By the oxidation of acetyltolthotoluidine we have, however, succeeded in obtaining acetyltolthoamidobenzoic acid.

Acetorthotoluidine was prepared by heating orthotoluidine (obtained from Kahlbaum) with glacial acetic acid for several hours, and recrystallising the product from aqueous alcohol, and was thus obtained in white needle-shaped crystals melting at 107—109°.

The oxidation of this compound offers no difficulty; for this purpose the acetotoluidine suspended in water was warmed on a water-bath and to it an aqueous solution of potassium permanganate was added in small quantities at a time, until its reduction was complete, as shown by the disappearance of the pink colour from the solution. The proportion of potassium permanganate was that of 2 mols. to 1 mol. of acetyltoluidine; the strength of the solution employed was about 10 grams per litre. It was found advantageous to add a little acetic acid to the permanganate solution, in order to neutralise the potash formed by its reduction, thus preventing the formation of toluidine and the products resulting from its oxidation. After the completion of the oxidation the manganese dioxide is removed by filtration, and the filtrate and wash waters are evaporated to a small bulk. On cooling, some unaltered acetyltoluidine separates out, the amount of which varied in different experiments from 5—20 per cent. of the acetyltoluidine employed. To the filtrate from the acetotoluidine a solution of lead acetate was added, by which means the acetylamidobenzoic acid is obtained in the form of lead salt. In one case the amount of lead salt obtained was about 60 per cent. of the theoretical quantity; the more general result was found to be a little above 30 per cent. of the theoretical.

Instead of precipitating the acid in form of lead salt, the filtrate from the unoxidised acetotoluidine may be treated with concentrated hydrochloric acid in the cold, whereby acetylamidobenzoic acid is obtained as a white crystalline precipitate, and in a state of perfect purity, as shown by its melting point. The quantity of acetylamidobenzoic acid obtained in this manner amounted to about 32 per cent. of the theoretical yield. Naturally this method is preferable to the precipitation of the acid as lead salt, since considerable loss is entailed in the conversion of the lead salt into the acid.

Acetyltolthoamidobenzoic acid, $C_6H_4.CO.OH.NH.Ac$ [1.2], may be

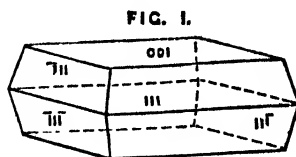
prepared in the manner already described, or from the lead salt by decomposing it whilst suspended in water, with sulphuretted hydrogen. The hot filtrate from the lead sulphide on cooling deposits the acid in white lustrous leaflets. It was then further purified by boiling its alcoholic solution with animal charcoal, and by evaporation of the alcoholic solution was obtained in white shining crystals which, after drying over sulphuric acid, gave the following analytical results:—

- (1.) 0.365 gram gave 0.1805 gram H_2O , and 0.802 gram CO_2 .
 (2.) 0.217 ,, 0.1005 gram ,, 0.4805 ,,
 (3.) 0.2335 ,, 0.1165 gram ,, 0.515 ,,

	Calculated.		Found.		
			(1.)	(2.)	(3.)
C ₉	108	60.34	59.97	60.37	60.12
H ₉	9	5.03	5.48	5.14	5.52
N	14	7.82	—	—	—
O ₃	48	26.81	—	—	—
	<hr/>	<hr/>			
	179	100.00			

Acetylorthoamidobenzoic acid is sparingly soluble in cold water, but largely in hot water and hot alcohol; on cooling it crystallises from these solutions in fine white lustrous leaflets, which when moist turn brown on exposure to the air: it melts at 179—180°. It dissolves easily in hot glacial acetic acid, and on cooling separates out in flat, long, colourless, transparent prismatic needles, which become opaque on exposure to the air. If the solution be allowed to stand and evaporate slowly these crystals disappear, the solution becoming slightly red or brown, and brownish-red well-defined crystals separate out. The colour is apparently due to oxidation by exposure to the air. For the following description of these crystals I am indebted to the kindness of Mr. Fletcher:—

“The crystals of this acid have in general the aspect of a square pyramid with two opposite vertices strongly truncated, as in Fig. 1:



on examination with the goniometer it is found that the pyramid does not quite accord with this hypothesis, the calculated angles of the section by the basal plane being 91° 2' and 89° 58' respectively in place of 90°. The faces have a common peculiarity of artificial

crystals, presenting a slight unevenness which results in the formation of multiple images when examined by reflected light.

"The system of crystallisation is the rhombic or prismatic, and the mean of what appeared to be the best angles gave $75^{\circ} 58'$ as the normal-angle between the basal plane and the predominant pyramid, while one of the lateral angles of this pyramid was determined to be $87^{\circ} 36'$.

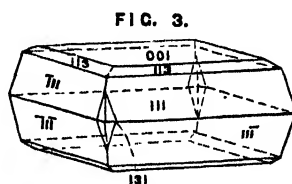
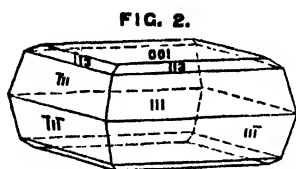
"From these the parametral angles are calculated to be—

$$010:011 \ 19^{\circ} 38'; \ 001:101 \ 70^{\circ} 42'; \ 100:110 \ 44^{\circ} 29',$$

and the parametral ratios—

$$a : b : c :: 0.982 : 1 : 2.803.$$

Developed in a less prominent degree are the pyramids (113) (131), as is shown in Figs. 2 and 3, while on one crystal the pyramid (133) was also observed.



"The following list of some of the principal angles of the crystal, as calculated from the above parameters, and as observed on the better crystals, will show to what extent these parameters may be relied upon as defining the system of planes:—

Angles.	Calculated.	Observed.
001.111	* $75^{\circ} 58'$	$75^{\circ} 58'$ mean
111.111	* $87 \ 36$	$87 \ 36$ „
111.111	$85 \ 10$	$84 \ 52$ — $85^{\circ} 25'$
111.111	$28 \ 4$	$28 \ 3, 28 \ 7$
001.113	$53 \ 8$	$53 \ 18, 53 \ 37$
111.113	$22 \ 50$	$22 \ 51, 22 \ 56$
111.131	$27 \ 23$	$27 \ 20, 27 \ 27$
001.131	$83 \ 35$	$83 \ 33, 83 \ 34$
111.131	$33 \ 31$	$33 \ 45$ —
111.131	$63 \ 32$	$63 \ 28$ — $64 \ 5$
001.133	$71 \ 21$	$71 \ 22$ — „

Acetylortho-amidobenzoic acid is easily converted into the ortho-amidobenzoic acid hydrochloride by boiling with concentrated hydrochloric acid or by saturating the alcoholic solution with hydrochloric acid gas and evaporating the solution. The hydrochloride thus ob-

tained gave, on decomposition with ammonia and acetic acid, *ortho*-amidobenzoic acid, melting at 144° . We have thus a ready method of obtaining *ortho*-amidobenzoic acid from orthotoluidine.

Lead acetylortho-amidobenzoate, $(C_6H_4NH\bar{A}c.CO_2)_2Pb$, obtained in the manner already described, was purified by boiling it repeatedly with hot water and allowing the filtrates from the undissolved portions to cool. It then separates out in white flocculent masses; it is sparingly soluble in hot and insoluble in cold water; strong acetic acid dissolves it, and is reprecipitated from this solution by water. Its analysis gave the following results: 0.328 gram of the salt gave 0.1055 gram of lead sulphate and 0.048 gram of lead, corresponding to 36.58 per cent. of lead, whilst theory requires 36.86 per cent.

Silver acetylortho-amidobenzoate, $C_6H_4.NH\bar{A}c.CO_2Ag$, is obtained as a white precipitate by adding silver nitrate to a solution of the ammonium salt. It is insoluble in cold water, but more soluble in hot water than the lead salt. From its solution in hot water it crystallises in fine white needles, often concentrically grouped, which turn brown on exposure to the air. The silver determination gave the following result:—

0.243 gram silver salt gave on ignition 0.0908 gram silver, corresponding to 37.36 per cent. of silver, whilst the formula requires 37.76 per cent. of silver.

These are the most characteristic salts of this acid. The barium, potassium, and sodium salts may be obtained as white crystalline powders by boiling the alcoholic solution of the acid with the respective carbonates; easily soluble in water and aqueous alcohol, but sparingly soluble in absolute alcohol.

An aqueous solution of the sodium salt gave the following reactions:—

With copper acetate, a turbidity; with silver nitrate, a white precipitate, which dissolved on boiling. Lead acetate gave no precipitate at first, but on shaking a white precipitate is obtained which is partially dissolved on boiling, and is soluble in strong acetic acid. With calcium chloride, no precipitate; on the addition of alcohol, a white precipitate is obtained. Zinc acetate behaved similarly to calcium chloride. Ferric chloride gave a yellowish-brown precipitate which is dissolved by acetic acid.

Diacetylortho-amidobenzoic acid, $C_6H_4N(\bar{A}c)_2CO_2H$ [2.1], is apparently produced when *ortho*-amidobenzoic acid (m. p. 144°) is heated with acetic anhydride in a vessel connected with a reversed condenser. On cooling, the whole solidifies to a crystalline mass, which was purified by boiling with alcohol and animal charcoal, and obtained in white

crystals, melting at about 220° . If dissolved in ammonia and the solution evaporated to dryness to expel the excess of ammonia, on taking up the residue with water a portion separates out, and the remainder is in solution as ammonium salt. This solution when treated with silver nitrate gives a curdy precipitate of the silver salt, the determination of the silver in which gave the following result:—

0.9385 gram of silver salt gave 0.305 gram of silver, corresponding to 32.49 per cent. Ag, whilst $C_6H_4N\bar{A}c_2.CO_2Ag$ required 32.92 per cent. of silver.

LXXII.—*Fourth Report to the Chemical Society on "Researches on some Points in Chemical Dynamics."**

Section I. By C. R. ALDER WRIGHT, D.Sc. London, Lecturer on Chemistry; and E. H. RENNIE, M.A. (Sydney), B.Sc. (London), Demonstrator of Chemistry; in St. Mary's Hospital Medical School. Sections II and III. By C. R. ALDER WRIGHT and A. E. MENKE.

§ 1. *Reduction of Ferric Oxide by Hydrogen and by Carbon Oxide.*

THE experiments detailed in the Third Report render it of interest to examine the character of the curved surfaces obtained with metallic oxides other than copper oxide, indicating the relationships between time, temperature, and amount of deoxidation by various reducing agents. Accordingly, experiments were made with two samples of ferric oxide, of which one (No. 1) was prepared by long-continued calcination of recrystallised ferrous sulphate, the powdered product being finally strongly heated in a combustion-tube in a current of air for many hours; this substance yielded 69.76 per cent. of Fe on reduction in hydrogen ($Fe_2O_3 = 70.00$ per cent.). The other specimen (No. 2) was prepared by peroxidising ferrous sulphate solution with nitric acid, pouring hot into excess of dilute ammonia, thoroughly washing, and drying at 100° ; the product yielded 60.29 per cent. of Fe on ignition in hydrogen, indicating a composition near to $2Fe_2O_3.3H_2O$, which would require 59.89 per cent. No trace of ferrous oxide was present in this substance, but a minute amount of highly basic sulphate was subsequently found in it; its texture was much more dense and compact than that of the "precipitated ferric oxide" examined in Report I, for which reason the temperatures at which reduction of this second sample by hydrogen and carbon oxide first commenced to be just manifest after a few minutes' action were perceptibly higher

* First Report: this Journal, January, 1878; Second Report, December, 1878; Third Report, August, 1879.

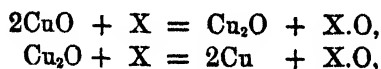
than those observed with the former specimen, the following values being deduced from a number of observations, the test employed being the decolorisation of permanganate after solution in hydrochloric acid and dilution with water.

Reducing agent.	Temperature of initial action (in 15 minutes).	
	Former specimen of precipitated ferric oxide.	New specimen, No. 2.
Carbon oxide	90°	136°
Hydrogen.....	195	230

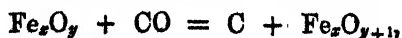
The calcined ferrous sulphate specimen (No. 1) was also more dense and compact, through longer heating, than the corresponding substance examined in Report No. I. Not only were the temperatures of initial action of hydrogen and carbon oxide somewhat higher accordingly, but further, much less differences were noticed between the temperatures at which these two reducing agents began to act after short periods of time with the newer specimen than with the old one: indeed, when the time did not exceed a few minutes, the difference was practically inappreciable. Thus the following temperature-values were deduced from a number of observations:—

Reducing agent.	Temperature of initial action (in 15 minutes).	
	Former specimen.	New specimen, No. 1.
Hydrogen.....	260°	270°
Carbon oxide	202	270

As pointed out in Report III, the action of carbon oxide on ferric oxide, unlike that of carbon oxide on copper oxide, is not strictly comparable with that of hydrogen, for whereas when copper oxide is reduced the sole actions taking place are expressed by the equations—



whether X be H_2 or CO, the actions taking place when ferric oxide is reduced are not identical when hydrogen is the reducing agent with those taking place with CO; in the former case the action is analogous to that indicated by the above equations, the higher oxide being reduced to a lower one, and finally to metal; with CO as reducing agent, however, as Lowthian Bell has shown, there is always a tendency to a reaction of a totally different kind, viz:—



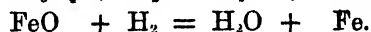
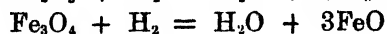
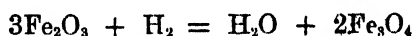
a lower oxide of iron being first formed, and subsequently becoming oxidised to a higher oxide, and carbon being set free; hence it is quite to be anticipated that the greater reducing power of CO, as compared with hydrogen due to the greater development of heat during its oxidation, would be more or less neutralised or diminished in the case of iron oxide by the tendency towards the reoxidation of the partially reduced substance in accordance with the above reaction. Notwithstanding this, however, the numbers detailed below show that the surface indicating the relations between time temperature and amount of deoxidation obtained by reducing ferric oxide with CO, lies outside (save at a very few points only) the analogous surface obtained with hydrogen, just as is the case with copper oxide, as shown in Report III.

In Report I it was shown that the temperatures of initial action of hydrogen on three specimens of Fe_2O_3 , Fe_3O_4 , and FeO , prepared by ignition processes, and presumably in approximately the same physical conditions, were respectively near to 260° , 290° , and 305° , *i.e.*, that the differences in temperature of initial action are not greater than may be accounted for by difference in physical state, and therefore that these differences do not afford any ground for supposing that the heat of formation of one oxide of iron is materially different from that of another, when reckoned per given amount of oxygen added on; whilst again Julius Thomsen's determinations of the heat of formation of ferrous and ferric hydrates being respectively 68,280 and 63,710 per 16 grams of oxygen, lead to the same conclusion. Such differences as were observed with the three oxides, however, point to the heat of formation of Fe_2O_3 being somewhat less than that of the lower oxides, whilst Thomsen's numbers also point in the same direction, the indication being much intensified if from Thomsen's numbers the values be calculated representing the heat evolved (per equal quantities of oxygen added on) in converting ferrous into ferric oxide, thus:—

Heat evolved in adding on 48 grams of oxygen forming (hydrated) Fe_2O_3	191,130
Heat evolved in adding on 32 grams of oxygen forming (hydrated) 2FeO	136,560
Difference approximately = heat evolved in transform- ing 2FeO into Fe_2O_3	54,570

or about 20 per cent. less than the heat of formation of Fe_2O_3 per 16 grams of oxygen added on. It is evident that the character of the curves indicating for given temperatures the amounts of deoxidation produced in given times under constant conditions will vary according as the heat absorbed in deoxidising a higher oxide to a lower

one, and that in reducing this lower one to a lower one still, and so on, are equal or not; if equal, curves will be obtained like those described in Report III, obtained with copper, no sharp or sudden alteration in the direction taken by the curve, no angle in short, being noticeable; if unequal, a more or less marked alteration in the curve must be indicated at points corresponding to the lower oxide, the further oxidation of which evolves less heat than its own heat of formation. For instance, if, as the above reasoning would seem to indicate may be the case, some or all of the reactions,



correspond to different heat evolutions, the difference should correspond to one or more angles in the curves lying near the points corresponding to Fe_3O_4 or FeO . On tracing out the curves experimentally, it is evident that a perceptible angle exists at the point corresponding to Fe_3O_4 , but none at that corresponding to FeO ; indicating that the amounts of heat given out per given quantity of oxygen taken up in the synthesis of FeO , and in the formation of Fe_3O_4 from FeO , are about equal; but that the heat given out in the formation of Fe_2O_3 from Fe_3O_4 is perceptibly smaller in amount.

Reduction of Fe_2O_3 (No. 1) from ignition of Ferrous Sulphate by Hydrogen.

The experiments were carried out in precisely the same way as those with copper oxide described in Report III, the loss of weight of a given quantity of oxide being determined after exposure for a known time to a given temperature; the only difference was that the quantity of ferric oxide used was smaller than that of the copper oxide formerly employed, on account of its greater bulkiness, the weight of Fe_2O_3 , occupying the same space as the 1.15 grams of CuO formerly used, being 0.43 gram. The hydrogen current employed was precisely the same as that used before, viz., 12.5 c.c. of gas at 0° and 760 per minute (100 bubbles per minute with the bubble apparatus used), or 0.00112 gram of hydrogen per minute, capable of removing from 0.43 gram of Fe_2O_3 , $\frac{0.00112 \times 8}{0.43} \times 100 = 2.08$ per cent. of oxygen per minute, out of the 30 per cent. present, i.e., requiring 14.5 minutes to produce complete deoxidation, supposing all the hydrogen to be converted into steam. The following values were obtained in four series of observations, made respectively at temperatures very close to 280° (hot air bath), 300° (diphenylamine vapour, not perfectly pure), 360°

(mercury vapour), and 420° (sulphur vapour). In each case it is noticeable that the difference between the numbers obtained by uninterrupted exposure for a given time, and those by successive exposure for shorter times jointly amounting to the same total time, do not differ largely from one another, practically the same mean curve being deducible from each set, just as with copper oxide.

Values obtained at 360° .

Time in minutes.	Percentage of oxygen removed.									
5	1.72	—	—	—	—	—	—	—	—	—
10	—	3.50	—	—	—	—	—	—	—	—
20	3.68	3.96	4.15	—	—	—	—	—	—	—
30	—	4.43	4.62	4.37	—	—	—	—	—	—
60	—	—	—	—	4.97	—	—	—	—	—
90	—	7.46	—	—	—	—	—	—	—	—
120	—	—	—	—	7.91	9.40	7.15	—	—	—
180	—	—	—	—	10.63	12.38	—	—	—	—
210	—	—	—	—	—	—	—	11.06	—	—
240	—	—	—	—	—	—	—	—	—	—
270	—	—	—	15.90	—	—	12.60	—	14.00	—
300	—	—	—	—	14.93	—	—	—	—	—
360	—	—	—	—	—	—	—	—	17.16	—
420	—	—	—	—	—	—	—	20.41	—	—
480	—	—	—	—	—	—	—	—	—	25.34
										27.62

It is noticeable that at the end of ten minutes the ferric oxide employed was so completely converted into Fe_3O_4 that the whole of the substance was readily attracted by a magnet from one part of the tube to another.

These numbers yield the following averages, from which the accompanying mean curve values are deduced:—

Time in minutes.	Un- interrupted observations.	Interrupted obser- vations.	Mean curve values.		
			Redaction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	1·72	—	1·72	1·72	0·344
10	3·50	—	3·50	1·78	0·356
20	4·15	3·82	3·92	0·42	0·042
30	4·87	4·52	4·35	0·43	0·043
60	4·97	—	5·65	1·30	0·043
90	—	7·46	7·00	1·35	0·045
120	8·27	7·91	8·35	1·35	0·045
180	—	11·50	11·10	2·75	0·046
210	11·06	—	12·50	1·40	0·047
240	14·00	14·25	14·00	1·50	0·050
270	—	14·93	15·55	1·55	0·052
300	17·16	—	17·16	1·61	0·054
360	—	20·41	20·70	3·54	0·059
420	25·34	—	24·70	4·00	0·066
480	—	27·62	27·62	2·92	0·049

Similarly the following numbers were obtained at 420°; to save space only the averages of the observed values are given; the uninterrupted and interrupted observations gave sensibly the same curve, and are used together in obtaining the averages:—

Time in minutes.	Average observed reduction.	Mean curve values.		
		Redaction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	4·09	4·10	4·10	0·82
10	4·55	4·75	0·65	0·13
15	5·73	5·40	0·65	0·13
35	7·95	8·20	2·80	0·14
60	13·60	12·20	4·00	0·16
75	13·65	14·70	2·50	0·167
90	15·90	17·25	2·55	0·17
120	22·67	22·70	5·45	0·182
150	28·41	28·40	5·70	0·19
165	29·79	29·80	1·40	0·093

Similarly the following average values were obtained at 300°

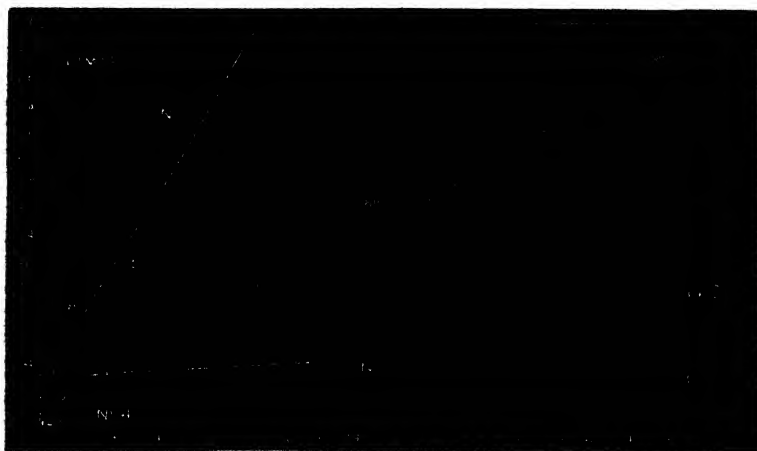
Time in minutes.	Average observed reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	0·23	0·20	0·20	0·04
10	0·46	0·50	0·30	0·06
15	1·14	1·15	0·65	0·13
20	2·06	2·10	0·95	0·19
25	3·25	3·25	1·15	0·23
30	3·30	3·30	0·05	0·010
40	3·59	3·35	0·05	0·005
60	3·48	3·47	0·12	0·006
90	3·78	3·65	0·18	0·006
180	4·35	4·20	0·55	0·006
300	5·04	5·05	0·85	0·007

At near 280° the following average numbers were deduced from a number of observations, the temperatures varying slightly in the different experiments, owing to the difficulty in keeping the air-bath at a perfectly constant temperature :—

Time in minutes.	Percentage of reduction.
10	Nil.
20	0·15
30	0·73

Fig. 1 exhibits the mean curves deduced from the above experiments, the continuous lined curves marked No. 1, No. 2, No. 3, and No. 4, representing respectively the values obtained at 360° , 420° , 300° .

FIG. 1.



and 280° . It is evident from inspection of these curves, firstly, that a marked angle or abrupt alteration of direction is noticeable when about 3·3 per cent. of oxygen had been removed (*i.e.*, when the Fe_2O_3 employed had been reduced to Fe_3O_4), this being specially marked in the case of curve No. 3; secondly, that no such angle is noticeable when about 10 per cent. of oxygen had been removed, *i.e.*, when the Fe_2O_3 had become reduced to FeO ; and thirdly, that the "chemical induction" or acceleration of rate of action noticed in Report III to occur with copper oxide is also noticeable with ferric oxide, both previously to and subsequently after the reduction of Fe_2O_3 to Fe_3O_4 .

On constructing a curved surface, indicating the relations between time, temperature, and amount of reduction in the way described in Report III, and taking sections from this surface, the following values are obtained :—

Amounts of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	At near 280° .	At 300° .	At near 360° .	At near 420° .
5	0	0·20	1·72	4·10
10	0	0·50	3·50	4·75
15	0·05	1·15	3·71	5·40
20	0·15	2·10	3·92	6·10
30	0·73	3·30	4·35	7·50
45	—	3·38	5·00	9·80
60	—	3·47	5·65	12·20
90	—	3·65	7·00	17·25
120	—	3·83	8·35	22·70
150	—	4·01	9·72	28·40
180	—	4·20	11·10	—
240	—	4·62	14·00	—
300	—	5·05	17·16	—
360	—	—	20·70	—
420	—	—	24·70	—
480	—	—	27·62	—

*Lengths of Time in Minutes required to produce given Amounts of
Deoxidation at different Temperatures.*

Percentage of oxygen removed (30 per cent. originally present).	Times.			
	At near 280°.	At 300°.	At 360°.	At 420°.
1	Upwards of 30	13	3	1
2	—	19	6	2
3	—	25	8	3
4	—	150	22	5
5	—	290	45	12
6	—	—	67	19
9	—	—	134	40
12	—	—	198	59
15	—	—	260	77
18	—	—	315	95
21	—	—	366	112
24	—	—	411	127
28	—	—	487	148

The times requisite to bring about complete deoxidation, were every trace of hydrogen converted into steam, would be, as above stated 14.5 minutes, so that to bring about reduction to Fe_3O_4 would require $\frac{14.5}{9} = 1.6$ minutes, under the same conditions, or about one-half the time actually required at 420°, one-fifth at 360°, and one-nineteenth at 300°.

On contrasting the curved surface thus constructed with the analogous one deduced for copper oxide (Report III), it is evident that the latter lies entirely outside the former; in other words, the "dynamic rule" arrived at in the previous Reports (that, *cæteris paribus*, the greater the algebraic value of the heat evolution taking place during the reduction of a metallic oxide by a given reducing agent, the lower the temperature at which the action commences) may be amplified thus, at least so far as the oxides of iron and copper and the reducing agents, hydrogen and carbon oxide, are concerned: *the greater the algebraic value of the heat evolution during reduction, the greater the amount of reduction in a given time at a given temperature, the less the time required to produce a given amount of reduction at a given temperature, and the lower the temperature required to produce a given amount of reduction in a given time.* The only point in which the above experiments with copper and iron oxides were not perfectly comparable was that owing to the difference in bulkiness between the two oxides the average weight of the former used for each observation was 1.15 gram,

and that of the latter 0.43 gram. The effect of using the larger quantity of copper oxide, however, would be simply (as shown in Report III) to make the rate of reduction somewhat less rapid than it would have been had only 0.43 gram been employed, and hence to diminish the difference between the actions on copper and iron oxide respectively.

Reduction of Fe_2O_3 No. 1 (from ignition of Sulphate) by Carbon Oxide.

The experiments just described were repeated, using CO instead of hydrogen, with the following results. It was found that when about 4 per cent. of oxygen was removed, deposition of carbon to a just appreciable extent usually commenced, the quantity formed increasing with the amount of deoxidation. Accordingly a number of determinations of the amount of carbon set free after given exposures were made, so as to obtain the data for correcting the observed losses of weight of the Fe_2O_3 employed by adding thereto the amount of carbon deposited, so as to obtain the amount of oxygen removed. These amounts of carbon were determined by sucking dilute hydrochloric acid into the tube containing the reduced Fe_2O_3 , and then washing out the contents without exposing them to air (sometimes the partially reduced Fe_2O_3 was pyrophoric, and hence loss of carbon by combustion during removal from the tube might have occurred had the contents of the tube been simply poured out). After boiling with stronger acid, the carbon was collected on a glass wool filter, washed, dried, and burnt in oxygen, and weighed as CO_2 . The quantities of carbon found to be produced per 100 parts of Fe_2O_3 employed varied between the following limits :—

Carbon deposited At 300°. Time.. Oxygen removed during this pe- riod	Nil	Trace to 0.25	0.25 to 1.0	1.0 to 3.15
	0 to 45 mins.	50 to 90 mins.	90 to 210 mins.	—
} 0 to 3.2 p. c.				
		3.4 to 4.4 p. c.	4.4 to 6.6 p. c.	—
At 360°. Time.. Oxygen removed	0 to 15 mins. 0 to 4.4 p. c.	15 to 25 mins. 4.4 to 6.0 p. c.	25 to 40 mins. 6.0 to 8.5 p. c.	40 to 95 mins. 8.5 to 17.2 p. c.
At 420°. Time.. Oxygen removed	0 to 10 mins. 0 to 5.9 p. c.	10 to 20 minutes. 5.9 to 9.4 per cent.		— —

The following values represent the average of a number of fairly concordant observations made at 300°, the uninterrupted observations and the interrupted ones (which gave practically the same mean curve), being used conjointly for the averages, and each

number being corrected for the amount of carbon deposited during the experiment:—

Time in minutes.	Average observed reduction (corrected).	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	0.40	0.30	0.30	0.06
10	0.57	0.60	0.30	0.06
15	0.86	0.90	0.30	0.06
20	1.72	1.25	0.35	0.07
30	1.90	2.00	0.75	0.075
45	3.11	3.20	1.20	0.080
60	3.84	3.80	0.60	0.040
90	4.15	4.37	0.57	0.019
120	5.34	4.94	0.57	0.019
210	6.64	6.64	1.70	0.019

Similarly the following are the average values obtained at 360°

Time in minutes.	Average observed reduction (corrected).	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	2.27	2.0	2.0	0.40
7	2.73	2.8	0.8	0.40
10	3.44	3.6	0.8	0.27
15	4.22	4.4	0.8	0.16
20	5.79	5.2	0.8	0.16
30	5.96	6.8	1.6	0.16
45	10.75	9.2	2.4	0.16
60	12.50	11.6	2.4	0.16
95	17.19	17.2	5.6	0.16

whilst the following average values were obtained at 420°:—

Time in minutes.	Average observed reduction (corrected).	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
3	2.52	2.55	2.55	0.85
5	4.11	4.15	1.60	0.80
10	5.43	5.90	1.75	0.35
15	8.54	7.65	1.75	0.35
20	9.40	9.40	1.75	0.35

At near 280° the following average numbers were obtained from several observations:--

Time in minutes.	Percentage reduction.
10	Nil.
20	0.07
30	0.49

The curves marked A, B, and C (dotted lines) in Fig. 1, respectively represent the above values obtained at 420°, 360°, and 300°. It is noticeable that whilst these curves (especially C) indicate an angle at a point close to that representing reduction to Fe_3O_4 , and whilst they respectively lie for the most part above the curves No. 2, No. 1, and No. 3, representing the reduction by hydrogen at these temperatures, yet a portion of curve C lies slightly below curve No. 3 (as also do the values obtained at 280° below curve No. 4), indicating that whilst the greater evolution of heat during the reduction by CO than during that by hydrogen caused the reducing action of CO to be on the whole more energetic *cæteris paribus* than that of hydrogen, yet the complicating circumstance that the action of CO is not of a purely reducing character, but is under certain conditions even oxidising in its nature (causing deposition of carbon and reoxidation of the lower iron oxide first formed), greatly diminished (with this particular sample of Fe_2O_3) the difference in reducing activity between CO and hydrogen, so much so as to cause the difference to be of reversed character for a certain small range of time and temperature variation, *i.e.*, for times not exceeding some 50 minutes, and for temperatures lying near to 300°.

The following tables represent the values obtained from the above numbers on constructing a curved surface, and taking sections therefrom as before:—

Amounts of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	At 280°.	At 300°.	At 360°.	At 420°.
5	0	0·30	2·00	4·15
10	0	0·60	3·60	5·90
15	0	0·90	4·40	7·65
20	0·07	1·25	5·20	9·40
30	0·49	2·00	6·80	—
45	—	3·20	9·20	—
60	—	3·80	11·60	—
90	—	4·37	16·40	—
120	—	4·94	—	—
210	—	6·64	—	—

Relations between Time in Minutes and Temperature requisite to produce given Amounts of Deoxidation.

Deoxidation. Percentage of oxygen re- moved.	Times.			
	At 280°.	At 300°.	At 360°.	At 420°.
1	Upwards of 30	17	2	1
2	—	30	5	2
3	—	42	8	3
4	—	71	12	5
5	—	123	18	8
6	—	176	25	11
7	—	229	31	14
8	—	—	37	16
10	—	—	49	22
12	—	—	62	—
14	—	—	75	—
16	—	—	88	—

On comparing this curved surface with that described in Report III, representing the reduction of copper oxide by CO, it is at once evident that the latter wholly lies outside the former, as might be anticipated from the results obtained with hydrogen above detailed.

Reduction of Fe₂O₃ No. 2 (precipitated and hydrated) by Hydrogen.

Accurate determinations by loss of weight being impracticable, owing to the presence of water of hydration in this sample of ferric oxide, the amount of deoxidation was determined by titration. To avoid pyrophoric reoxidation of the partially reduced substance

(which was found to be very apt to occur when some 4 per cent. or upwards of oxygen was lost), each U-tube was broken after the exposure in a clean porcelain basin, under a solution of copper sulphate mixed with ferric chloride, so that any metallic iron might reduce an equivalent amount of copper. The whole was then boiled with hydrochloric acid until completely dissolved, diluted with boiled and cooled distilled water, and titrated by permanganate. Owing to the trouble involved in each determination, the observations were not multiplied largely, some eight or ten only being made for each of the sets of which the following are the average results. This sample of ferric oxide being somewhat more dense than No. 1, the average weight used for each determination was greater, viz., 0.65 gram, containing 0.168 gram of oxygen as Fe_2O_3 , so that the current of hydrogen employed was capable of bringing about complete reduction in

$$\frac{0.168}{0.00112 \times 8} = 18.7 \text{ minutes.}$$

At 257° (*Cubeb Oil*).

Time in minutes.	Average deoxidation per 100 of precipitated ferric oxide.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
22.5	0.56	0.58	0.58	0.026
45	1.25	1.16	0.58	0.026
60	1.54	1.55	0.39	0.026
120	3.05	3.00	1.45	0.024
240	3.25	3.25	0.25	0.002

At 300° (*Diphenylamine*).

17.5	1.29	1.17	1.17	0.067
37.5	2.86	2.50	1.33	0.067
60	3.15	3.15	0.65	0.029
90	3.39	3.45	0.30	0.010
210	4.63	4.65	1.20	0.010

At 360° (*Mercury Vapour*).

15	2.60	2.60	2.60	0.173
20	3.19	3.19	0.59	0.118
30	3.40	3.40	0.21	0.021

These values indicate, like those obtained with ferric oxide No. 1, that the rate of reduction after 2.87 per cent. of oxygen is removed

(the quantity corresponding to complete reduction of the Fe_2O_3 , present in the hydrated substance to Fe_3O_4) is considerably slower than that previously existing, i.e., that the curves exhibit an angle at the point corresponding to Fe_3O_4 . These three mean curves are respectively indicated by curves Nos. 1, 2, and 3 in Fig. 2 (continuous lines).

FIG. 2.



On constructing a curved surface, and taking sections as before, the following values are obtained :—

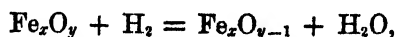
Amounts of Deoxidation produced in given Times at different Temperatures.

Time in minutes.	Temperatures.		
	At 257°.	At 300°.	At 360°.
5	0·13	0·33	0·87
10	0·26	0·67	1·73
15	0·39	1·00	2·60
20	0·52	1·33	3·19
30	0·78	2·00	3·40
45	1·16	3·00	—
60	1·55	3·15	—
90	2·33	3·45	—
120	3·05	3·75	—
150	3·10	4·05	—
180	3·15	4·35	—
210	3·20	4·65	—
240	3·25	—	—

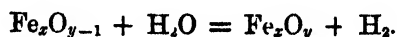
Lengths of Time in Minutes requisite to produce given Amounts of Deoxidation.

Deoxidation.	Times.		
	At 257°.	At 300°.	At 360°.
1	39	15	6
2	78	30	12
3	120	45	18
3·5	360	95	35
4	—	145	—

On comparing the surface thus traced out with the similar one obtained with ferric oxide No. 1, it is noticeable that whilst at temperatures below 300° reduction went on more rapidly with the precipitated oxide than with the ignited specimen, yet this did not hold good for higher temperatures. Owing to the difference in the quantities of oxygen existing as Fe_2O_3 in the equal bulks employed of the two specimens ($0.48 \times \frac{30}{100} = 0.129$ gram in the ignited sample, and $0.65 \times \frac{25.8}{100} = 0.168$ gram in the precipitated specimen), the two surfaces are not absolutely comparable with each other in all respects; but they are sufficiently nearly so to indicate that at temperatures upwards of 300° the rate of reduction of the ignited specimen was more rapid than that of the other, whilst even at 300° reduction to Fe_3O_4 ensued in about the same time with the ignited specimen as with the other when compared with the time requisite for complete reduction by the hydrogen current employed, assuming that all the hydrogen were converted into H_2O . With the ignited specimen as above stated, the time thus requisite for complete reduction would be 14.5 minutes, whence reduction to Fe_3O_4 would be possible in 16 minutes, or about one-nineteenth of the time actually employed. With the precipitated specimen the time thus requisite for complete reduction would be 18.7 minutes, whence reduction to Fe_3O_4 would be possible in 2.1 minutes, or about one-eighteenth of the time actually employed at 300° . In all probability the retarding influence thus indicated as existing at 300° and upwards in the case of the precipitated oxide is due to the action of the aqueous vapour expelled by the heat from the partial removal of the water of hydration; for doubtless the rate of reduction at any given point in the mass operated on is a function (*inter alia*) of the relative tensions of the hydrogen and the water vapour present, the former tending to reduce in virtue of the action—



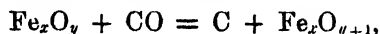
whilst the latter has more or less tendency to bring about the converse change—



Reduction of Ferric Oxide No. 2 (precipitated) by Carbon Oxide.

In order to avoid the great amount of loss of time and labour involved in the mode of observation just described, the following method was adopted. A weight of substance close to the average weight, 0.65 gram, was placed in the U-tube, and connected with the carbon oxide gasometer and purifiers, &c., on the one side, and with a calcium

chloride tube and potash bulbs on the other, and then immersed in the hot vapour bath. After a known time the potash bulb was exchanged for another, and so on, the amount of deoxidation being ultimately deduced from the quantities of CO_2 collected by taking four-elevenths of that amount as the O removed from the Fe_2O_3 . Additive corrections were made for the minute amounts of CO_2 remaining in the calcium chloride tube, &c., at the moment of exchanging the bulbs, based on direct determinations of the amounts at different stages of reduction; and when necessary subtractive corrections were also made for the amount of CO_2 collected, corresponding to the amount of carbon deposited in virtue of the reaction—



inasmuch as a portion of the four-elevenths of the weight of CO_2 collected represented oxygen derived not from the Fe_2O_3 , but from the CO reduced to carbon by that reaction. This latter correction, however, was always minute, even when sensible at all, as the quantities of carbon deposited were only very small, much smaller, in fact, than the amounts deposited with ferric oxide No. 1 for equal amounts of reduction. Thus the following table represents the carbon deposition observed (per 100 parts of hydrated Fe_2O_3 employed):—

Carbon deposited.....	Nil	Traces.	Trace to 0·2
At 184·5°. Time.....	0 to 240 minutes.	—	—
Oxygen removed during this period	} 0 to 3·6 per cent.	—	—
At 210°. Time	0 to 240 minutes.	—	—
Oxygen removed	0 to 3·75 per cent.	—	—
At 257°. Time	0 to 60 minutes.	60 to 120 minutes.	—
Oxygen removed	0 to 4·9 per cent.	4·9 to 9·2 per cent.	—
At 300°. Time	0 to 30 minutes.	30 to 60 minutes.	60 to 105 minutes.
Oxygen removed	0 to 5·0 per cent.	5·0 to 7·5 per cent.	7·5 to 10·9 per cent.

The following average corrected values were obtained at 184·5° (aniline vapour-bath):—

Time in minutes.	Average observed loss of oxygen (corrected).	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
30	1.37	1.3	1.3	0.043
60	2.30	2.4	1.1	0.037
90	2.85	3.0	0.6	0.020
120	3.10	3.12	0.12	0.004
180	3.37	3.36	0.24	0.004
240	3.57	3.60	0.24	0.004

Similarly the following numbers were obtained at 210° (naphthalene, at 257° (cubeb oil), and at close to 300° (diphenylamine).

At 210°.

Time in minutes.	Average observed loss of oxygen (corrected).	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
30	1.85	1.8	1.8	0.060
60	2.68	2.8	1.0	0.033
90	3.00	3.1	0.3	0.010
120	3.32	3.23	0.13	0.0043
180	3.52	3.49	0.26	0.0043
240	3.72	3.75	0.26	0.0043

At 257°.

15	1.65	1.6	1.6	0.107
30	2.85	2.9	1.3	0.087
60	4.85	4.9	2.0	0.067
90	6.99	7.0	2.1	0.070
120	9.24	9.2	2.2	0.073

At 300°.

15	3.06	3.1	3.1	0.207
30	5.12	5.0	1.9	0.127
60	7.68	7.5	2.5	0.083
90	9.87	9.8	2.3	0.077
105	10.86	10.9	1.1	0.073

These four mean curves are respectively represented by curves A, B, C, and D (dotted lines), Fig. 2. Like all the other curves, the rate of reduction after reduction to Fe_3O_4 is considerably slower than before, so that a more or less perceptible angle exists, corresponding to Fe_3O_4 .

On constructing a curved surface, and taking sections as before, the following values are obtained :—

Amounts of Reduction produced in given Times at different Temperatures.

Time in minutes.	Temperatures.			
	At 184.5°.	At 210°.	At 257°.	At 300°.
15	0.70	0.90	1.60	3.10
30	1.30	1.80	2.90	5.00
60	2.40	2.80	4.90	7.50
90	3.00	3.10	7.00	9.80
120	3.12	3.23	9.20	10.90
180	3.36	3.49	—	—
240	3.60	3.75	—	—

Lengths of Time in Minutes requisite to produce given Amounts of Deoxidation.

Deoxidation.	Times.			
	At 184.5°.	At 210°.	At 257°.	At 300°.
1	23	17	9	5
2	49	36	20	10
3	90	80	31	14
3.5	215	182	39	17
4	—	—	46	22
6	—	—	76	42
8	—	—	104	66
10	—	—	—	93

On comparing this surface with that obtained with this sample of ferric oxide and hydrogen, it is at once evident that the former lies wholly outside the latter. On comparing it with the surface obtained with ferric oxide No. 1 and CO, it is evident that the precipitated oxide is at all temperatures more rapidly reduced by CO than the ignited oxide, *i.e.*, that the evolution of aqueous vapour by heat from the precipitated oxide does not retard the reduction by CO as much as it does that by hydrogen, as might be anticipated *à priori*.

§ 2. *Relations between Time, Temperature, and Rate of Reduction of Manganese Dioxide by Hydrogen and by Carbon Oxide.*

The previous experiments having demonstrated that the points where an abrupt alteration occurs in the direction of the curve representing the rate of reduction under constant conditions correspond to

oxides, the formation of which generates a larger heat development (per given amount of oxygen) than does the formation of higher oxides, it is evident that the formation of oxides of manganese higher than MnO up to MnO_2 must give rise to less heat evolution (per equal weight of oxygen combined) than that of MnO itself; for, as has been demonstrated in Report II, MnO is wholly unaffected by either hydrogen or carbon oxide at temperatures far above those at which reduction of higher oxides of manganese takes place readily, this reduction, however, never proceeding further than the formation of MnO .* In order to trace out curves representing the correlations between time, temperature, and rate of reduction of manganese dioxide, and so to obtain evidence as to whether any marked differences exist between the heat evolutions corresponding to the formation of MnO_2 , Mn_3O_4 , Mn_2O_3 , and other oxides higher than MnO , a number of observations were made in precisely the same way as those heretofore described, employing a specimen of substance having approximately the composition of manganese dioxide prepared by heating on the water-bath potassium permanganate solution and nitric acid; this substance has already been described in a paper on Manganese Dioxide (this Journal, 1880, i, 29); it had a composition closely represented by the formula $32\text{MnO}_2 \cdot 2\text{MnO} \cdot \text{K}_2\text{O} \cdot 22\text{H}_2\text{O}$, containing 70.68 per cent. of MnO and 14.91 per cent. of available oxygen (average of several accordant determinations). The weight of this substance occupying the same bulk as the iron and copper oxides employed in the above-described experiments was close to 0.30 gram, which weight, therefore, represents approximately the quantity used for each observation. The hydrogen and carbon oxide currents used were identical with those employed before, viz., those capable of combining with 0.00896 gram of oxygen per minute. Since the manganese dioxide contained 14.91 of oxygen existing as higher oxide over and above that present as MnO , these currents would be capable of reducing 0.30 gram to MnO in $\frac{14.91 \times 0.3}{100 \times 0.00896} = 5.0$ minutes. In

order to determine the amount of reduction in each experiment, the partially reduced contents of the U-tube were carefully transferred to a flask and boiled with strong hydrochloric acid, and the evolved chlorine determined by reception in potassium iodide and titration by thiosulphate; the oxygen removed was then deduced by calculating the residual available oxygen per 100 of original substance, and subtracting from 14.91; the results thus obtained yielded the following averages.

* Julius Thomsen has shown (*Berichte*, 5, 176 (1872)) that the formation of manganic acid from MnO evolves no heat at all, whilst that of MnO_2 produces heat, and that of permanganic acid absorbs heat.

A. Reduction by Hydrogen. At 210° (Naphthalene Vapour).

In this series of experiments the numbers obtained by the titration method just described were checked by drying a portion of the substance in a current of air at 210° for several hours so as to expel all water of hydration capable of expulsion at that temperature, and then making observations of the loss of weight occasioned by heating for various periods in the normal current of hydrogen; the numbers thus obtained (calculated per 100 parts of undried substance) exhibited a fairly close agreement with those got by titrating the residual oxygen and subtracting the amount (calculated per 100 of original substance) from 14.91, the percentage of oxygen originally present. This method of observation, being probably less accurate than the titration method, was, however, not employed in any of the other series of observations. Twenty-four observations (twelve by each method) gave the following results:—

Time in minutes.	Reduction.		Mean curve values.		
	By titration.	By loss of weight.	Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	1.86	1.62	1.70	1.70	0.34
10	2.31	2.50	2.35	0.65	0.14
15	2.87	2.40	2.9	0.55	0.110
30	4.79	3.92	4.5	1.6	0.107
60	7.43	7.30	7.6	3.1	0.103
75	9.37	9.70	9.1	1.5	0.100
90	10.17	10.37	10.0	0.9	0.060
105	10.14	10.16	10.3	0.3	0.020
120	10.31	10.34	10.57	0.27	0.018
180	12.07	12.18	11.60	1.03	0.017
240	12.01	11.90	12.40	0.80	0.013
360	13.80	13.73	13.80	1.40	0.012

These numbers evidently indicate an angle in the curve at about the point corresponding to the composition Mn_3O_4 ; as the substance originally contained 11.91 per cent. of available oxygen and 70.68 per cent. of MnO , reduction to Mn_3O_4 would be brought about when the substance contained 5.31 oxygen per 100 of original substance, i.e., when 9.60 per cent. of oxygen had been removed: it is manifest that the rate of reduction abruptly diminished when about this quantity of oxygen had been lost.

At a somewhat higher temperature the same phenomenon was noticeable, but to a less distinctly marked extent : thus the following average numbers were obtained :—

At 257° (Cubeb Oil).

Time in minutes.	Reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
5	2·77	2·77	2·77	0·544
15	6·45	6·45	3·68	0·368
30	11·17	11·17	4·72	0·315
60	14·71	14·71	3·54	0·118

At 184·5 the amount of reduction approximated towards the composition Mn_3O_4 after four hours' action, but only just reached that amount in six hours.

At 184·5° (Aniline Oil).

Time in minutes.	Reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
15	2·63	2·6	2·6	0·173
30	3·41	3·4	0·8	0·053
60	4·29	4·55	1·15	0·038
90	5·61	5·6	1·05	0·035
120	6·56	6·6	1·00	0·033
180	7·52	7·75	1·15	0·019
240	8·89	8·85	1·10	0·018
360	9·63	9·63	0·78	0·0085

Evidently in this instance also the rate of reduction of the higher oxide to Mn_3O_4 is considerably greater than that of the Mn_3O_4 produced, indicating an angle in the curve at that point.

At 160° the rate of reduction was not nearly sufficiently rapid to cause reduction to Mn_3O_4 in six hours.

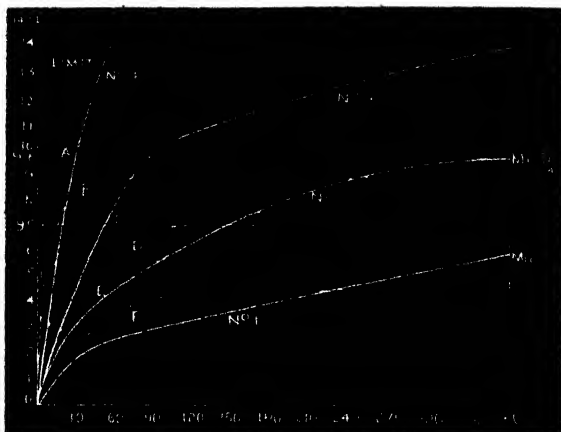
At 160° (Turpentine Vapour).

Time in minutes.	Reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
30	1·94	1·9	1·9	0·063
60	2·86	2·4	0·5	0·017
120	2·85	3·2	0·8	0·013
240	5·30	4·7	1·5	0·0125
360	5·44	5·44	0·74	0·0062

It is evident that the above numbers, whilst indicating an angle in the curve line at a point corresponding to Mn_3O_4 , afford no indication of any angle at points representing oxides lying between Mn_3O_4 and MnO_2 , *e.g.*, Mn_2O_3 , which would represent a removal of 6·95 per cent. of oxygen (leaving 7·96 per cent., corresponding to 70·68 per cent. MnO): it has also been shown (Report II, this Journal, December, 1878) that the reduction of higher oxides of manganese by hydrogen stops altogether when the composition MnO is attained, whence the composition evidently represents another angle: hence, finally, it may be concluded that the curve lines representing the reduction of MnO_2 by hydrogen contain altogether two, and only two angles or points of abrupt alteration of rate of reduction: the one corresponding to the composition MnO , the other to Mn_3O_4 ; whence it may be deduced that the heat of formation of MnO (per given quantity of oxygen added to manganese) is greater than that of Mn_3O_4 , which again is greater than that of any higher oxide. That Mn_3O_4 is far more stable when heated *per se* than any higher oxide is well known; thus, as is well known (compare also Report II), *strong* ignition in air of any higher oxide gives rise to Mn_3O_4 with expulsion of oxygen, but not to any oxide lower than Mn_3O_4 . Doubtless the ready conversion of Mn_3O_4 into an indefinite higher oxide by *gentle* heating in air, and the dependence of the amount of oxygen thus taken up on the tension of the oxygen on the surrounding atmosphere (Dittmar, this Journal, 1864, 294), is correlated with the approximately equal heats of formation of all oxides higher than Mn_3O_4 as indicated by the absence of angles in the above curves at points representing these oxides.

The four mean curves just described are represented in Fig. 3, the continuous lines marked Nos. 1, 2, 3, and 4 respectively representing the curves obtained at 160°, 184·5°, 210°, and 257°.

FIG. 3.



On constructing a curved surface and taking sections, the following values are obtained :—

Amounts of Reduction produced in given Times at different Temperatures.

Time in minutes.	Temperatures.			
	At 160°.	At 184.5°.	At 210°.	At 257°.
5	0.5	1.1	1.7	2.8
10	0.9	1.9	2.35	4.7
15	1.2	2.6	2.9	6.45
20	1.45	2.9	3.5	8.2
30	1.9	3.4	4.5	11.2
60	2.4	4.55	7.6	14.7
75	2.6	5.1	9.1	—
90	2.8	5.6	10.0	—
120	3.2	6.6	10.6	—
180	4.0	7.75	11.6	—
240	4.7	8.85	12.4	—
360	5.4	9.6	13.8	—

Lengths of Time in Minutes requisite to produce given Amounts of Reduction.

Percentage of oxygen removed.	Time.			
	At 160°.	At 184·5°.	At 210°.	At 257°.
1	11	4	3	2
2	35	11	7	4
3	105	22	16	6
4	180	45	25	8
5	290	72	34	11
6	—	100	45	14
8	—	190	63	18
10	—	400	90	25
12	—	—	210	35
14	—	—	380	55

B. Reduction by Carbon Oxide.

The following average numbers were obtained by the titration method :—

At 100° (Water Vapour).

Time in minutes.	Reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
15	1·18	1·18	1·18	0·079
30	2·17	2·17	0·99	0·067
60	3·58	3·58	1·41	0·047
120	4·46	4·42	0·84	0·014
240	4·54	4·58	0·16	0·0018
360	4·71	4·71	0·13	0·0011

At 130° (Fusel Oil).

15	3·69	3·4	3·4	0·227
30	4·01	4·2	0·8	0·053
60	5·19	5·0	0·8	0·026
120	5·62	5·6	0·6	0·010
240	5·94	6·0	0·4	0·0033
360	6·37	6·3	0·3	0·0025

At 140—141° (*a Petroleum Distillate Vapour*).

Time in minutes.	Reduction.	Mean curve values.		
		Reduction.	Difference.	Rate of reduction per minute in each consecutive interval of time.
2	1.20	1.3	1.3	0.650
5	3.32	3.0	1.7	0.567
10	3.52	3.8	0.8	0.160
15	4.27	4.3	0.5	0.100
30	5.08	5.2	0.9	0.060
60	6.68	6.5	1.3	0.043
90	6.41	6.85	0.35	0.012
120	6.80	7.0	0.15	0.005
180	7.45	7.1	0.1	0.0017
240	7.34	7.15	0.05	0.0008
360	7.04	7.2	0.05	0.0004

In these experiments it is evident that the rate of reduction slackened much more rapidly than was the case in the corresponding experiments with hydrogen; so much so, that in the last case when nearly one-half of the available oxygen present was removed, the rate of reduction became so slow (doubtless owing to the difficult penetration of the CO into the interior of the particles through the formation of a film of Mn_3O_4 on the outside) that the experimental errors attaching to the method of observation became greater than the amounts of reduction deduced by taking the differences between the separate observations. At higher temperatures still this became even more marked; thus the following values were obtained in nine observations at 160° (turpentine vapour), seven at 184.5° (aniline), and five at 210° (naphthalene):—

At 160°.		At 184.5°.		At 210°.	
Time.	Percentage of reduction.	Time.	Percentage of reduction.	Time.	Percentage of reduction.
5	3.48	5	3.63	10	10.01
15	6.26	20	7.79	30	10.97
30	6.22	30	9.86	90	10.16
60	7.65	60	9.05	180	9.93
120	7.40	120	8.16	360	10.07
180	7.24	240	9.01		
		360	9.40		

That is, the rate of reduction became so small as to be barely perceptible, if not masked altogether by experimental error, when a certain amount of oxygen had been removed, this amount being less the lower the temperature, viz. :—

At 100°	in about 240 minutes	when about 4.5	} per cent. was removed.
„ 130	„ 240	„ „ 6.0	
„ 140—141	„ 120	„ „ 7.0	
„ 160	„ 60	„ „ 7.5	
„ 184.5	„ 30	„ „ 9.0	
„ 210	„ 10	„ „ 10.0	

It is noticeable that these two last values are close to the point where all the manganese present existed as Mn_3O_4 , this corresponding, as above shown, to a removal of 9.60 per cent. : owing, however, to the reduction practically coming to a stop at lower temperatures before this point was reached, this circumstance is not of much weight as indicating an angle in the manganese curve at the point corresponding to Mn_3O_4 .

The dotted lines, A, B, C, D, E, F, in Fig. 3 represent respectively the mean curves deduced as above for 210°, 184.5°, 160°, 140—141°, 130°, and 100°, the latter three being drawn as straight lines in the later periods of time, the rate of reduction having become too small to measure accurately.

On constructing a curved surface with these curves, and taking sections, the following values are obtained :—

Amounts of Reduction produced in given Times at different Temperatures.

Time in minutes.	Temperatures.					
	100°.	130°.	140—141°.	160°.	184.5°.	210°.
5	0.4	1.5	3.0	3.5	3.6	—
10	0.8	2.6	3.8	5.0	—	10.0
15	1.2	3.4	4.3	6.0	—	—
20	1.6	3.7	4.7	6.1	7.8	—
30	2.2	4.2	5.2	6.4	9.0	—
60	3.6	5.0	6.5	7.5	—	—
120	4.4	5.6	7.0	—	—	—
180	4.5	5.8	—	—	—	—
240	4.6	6.0	—	—	—	—
360	4.7	6.3	—	—	—	—

Lengths of Time in Minutes requisite to produce given Amounts of Reduction.

Reduction.	Temperatures.					
	100°.	130°.	140—141°.	160°.	184·5.	210°.
per cent.						
1	12	3	2	1	1	—
2	27	7	4	3	2	—
3	50	13	5	4	4	—
4	90	25	12	7	—	—
5	upwards of 360	60	25	10	—	—
6	"	240	50	15	—	—
7	"	upwards of 360	120	45	—	—
8	"	"	upwards of 360	upwards of 180	22	—
9	"	"	—	—	30	less than 10
10	"	"	—	—	upwards of 360	10
11	"	"	—	—	—	upwards of 360

On comparing this surface with that previously obtained with hydrogen, it is noticeable that whilst the CO surface lies outside the hydrogen surface (as it should do in accordance with the previously detailed experiments on iron and copper oxides) for a considerable extent, yet it does not wholly do so; the cause of this is doubtless the lower diffusibility of CO as compared with hydrogen; the latter lighter gas passes more readily through the film of reduced oxide coating the particles experimented with, and hence causes the reduction to go on more readily (other things being equal) than would be the case with the heavier CO: similarly the resultant water vapour produced by the action of the hydrogen diffuses away more rapidly than the CO₂ formed by the CO. As pointed out in Report III, it is impossible to equalise completely all the conditions in making experiments with different reducing gases; as long, however, as interfering and perturbing causes do not come too largely into play, the reduction of manganese dioxide follows the same general law as has been deduced from the behaviour of iron and copper oxides, viz., that "the greater the development of heat (algebraically) in the action, the greater is the amount of deoxidation in a given time at a given temperature, the less the time required for the production of a given amount of reduction at a given temperature, and the lower

the temperature requisite to produce a given amount of reduction in a given time."

§ 3. *Relations between Time, Temperature, and Rate of Oxidation of Spongy Metallic Copper by Hot Air.*

The preceding experiments having indicated, amongst other things, that the rate of reduction of a given metallic oxide by a gaseous reducing agent is considerably affected by the power possessed by that agent of diffusing through the film of partially reduced substance formed on the outside of the particles of substance used, it was thought desirable to try some experiments of a converse character, viz., experiments on the rate of oxidation of a metal by oxygen. For convenience, ordinary air (purified by passage through sulphuric acid, caustic potash, and silver nitrate pumice-stone tubes, and dried by calcium chloride) was used instead of oxygen; the metal chosen was spongy copper prepared by reducing in pure hydrogen at a temperature of about 185°, copper oxide made by igniting copper nitrate from electrolytic copper, and finely powdering the mass. After several hours' action and frequent intermixture, the resultant metal lost only 0.31 per cent. on ignition in hydrogen, i.e., it contained 99.69 per cent. of copper: the substance thus obtained was not in the slightest degree pyrophoric, and could be kept unchanged in a stoppered bottle for months. Evidently, if such a substance be subjected to the action of a constant current of air at a constant temperature for various times, the rate of oxidation might be expected, *à priori*, to diminish gradually as the time increases (apart from possible "chemical induction" just at first); for the diffusibility of air being much the same as that of carbon oxide, the formation of a film of oxide on the outer surface of the particles of metal might be expected to cause the same kind of retardation as has been noticed in the above-described reduction experiments. The experiments with manganese dioxide described in the last section, moreover, render it probable that the point at which the rate of action becomes very small (not greater than the experimental errors), will vary with the temperature, the action stopping (or nearly so) at a point representing an amount of oxidation the larger the higher the temperature. These *à priori* indications were realised completely on trying the experiments.

The same sized U-tubes were used for these experiments as for those previously described on the reduction of metallic oxides; the average weight of finely divided metal used for each experiment was 1.02 grams. The air current employed was produced by an aspirator on the principle of Bunsen's pump: by sucking in air from graduated tubes it was found that the rate of bubbling through the particular

bubble apparatus used (100 bubbles at 15° to 20° per minute) represented very close to 13·5 c.c. of air at 0° and 760 per minute; so that 2·82 c.c. of oxygen weighing 0·00403 gram passed per minute. Hence

this current could add on to 1·02 gram of copper $\frac{0\cdot00403}{1\cdot02} \times 100 =$

0·395 per cent. per minute of oxygen, or almost precisely equal to the maximum rate of oxidation observed (in experiments at 210° and upwards). In these experiments the copper nearest to the aspirator in the U-tube remained bright during the first few minutes of action whilst the middle portion became covered with an iridescent film, and the portion nearest the entering air current became discoloured and brown; so that in this case the oxygen was evidently absorbed as rapidly as supplied, only nitrogen passing onwards. After a little time, however, the whole of the copper became discoloured and then the rate of oxidation began to diminish, gradually slackening until it practically ceased. In experiments at lower temperatures the same kind of thing was noticeable, only the whole of the oxygen supplied was never absorbed, and the copper became iridescent or discoloured throughout accordingly, instead of only at the entrance end of the U-tube. At 100° no action whatever was noticeable, even after many hours; at 130° indications of chemical induction were observed, no action whatever being observed for upwards of two hours, after which slight discoloration and increase of weight became perceptible at a slightly increasing rate. At 160° these indications were still more strongly marked, but at 184·5° and upwards the maximum rate of oxidation occurred at first, no indications of induction being traceable. The following values were obtained at 210°; just as with most of the experiments on reduction, no difference in the amount of action was noticeable whether the U-tube were exposed for an uninterrupted time T, or interruptedly for a series of smaller times jointly equal to T:—

Oxygen added on per 100 parts of metallic copper employed.														Mean curve values.			
Time in minutes.													Average.		Oxidation.	Difference.	Oxygen added per minute in each con- secutive interval of time.
													Uninter- rupted.	Inter- rupted.			
2	0.78	0.80												0.79	0.79	0.79	0.395
3	—	—	1.20	—	—	—	—	—	—	—	—	—	—	1.20	1.18	0.39	0.390
5	2.15	—	—	1.52	—	—	—	—	—	—	—	—	1.61	2.15	1.80	0.62	0.310
6	—	—	2.05	—	—	—	—	—	—	—	—	—	—	2.05	2.00	0.20	0.200
10	—	—	2.40	2.35	—	—	—	—	—	—	—	—	2.44	2.38	2.42	0.42	0.105
15	—	—	—	2.70	2.60	—	—	—	—	—	—	—	2.60	2.62	2.70	0.28	0.086
20	—	—	3.00	—	—	3.00	—	—	—	—	—	—	3.00	3.00	2.90	0.20	0.040
30	2.98	3.01	—	3.00	3.10	—	3.10	—	—	—	—	—	3.10	3.06	3.20	0.30	0.080
45	—	—	—	—	—	3.39	—	—	—	—	—	—	—	3.35	3.45	0.25	0.017
60	—	3.54	—	—	—	—	3.65	3.59	3.59	—	—	—	3.59	3.54	3.60	0.15	0.010
90	—	—	—	—	4.05	—	3.80	3.79	3.83	3.83	—	—	3.78	3.88	3.85	0.25	0.008
150	—	—	—	—	4.55	—	—	4.20	—	4.30	4.30	—	—	4.35	4.25	0.40	0.007
210	—	—	—	—	4.55	—	—	4.70	—	4.60	4.60	—	—	4.45	4.60	0.35	0.006
270	—	—	—	—	—	—	—	—	—	4.64	—	—	—	4.67	4.90	0.30	0.005
330	—	—	—	—	—	—	—	—	5.39	—	—	—	—	5.39	5.15	0.25	0.004

In just the same way the following average numbers were obtained at 184·5° in an aniline vapour-bath:—

Time in minutes.	Reduction.		Mean curve values.		
	Uninterrupted.	Interrupted.	Oxidation.	Difference.	Oxygen added on per minute in each consecutive interval of time.
5	0·66	—	0·60	0·60	0·120
10	0·81	0·86	0·90	0·30	0·060
15	1·15	1·10	1·12	0·22	0·044
20	—	1·22	1·30	0·18	0·036
30	1·60	1·54	1·57	0·27	0·027
45	—	2·10	1·90	0·33	0·022
60	2·20	2·27	2·18	0·28	0·019
90	—	2·76	2·64	0·46	0·015
120	—	2·95	2·96	0·32	0·011
150	—	3·15	3·20	0·24	0·008
180	3·20	3·39	3·39	0·19	0·0063
240	—	3·60	3·65	0·26	0·0045
360	—	3·86	3·85	0·20	0·0033

At 360° (mercury vapour) the following numbers were obtained, the average of all the observations (uninterrupted and interrupted) being taken together:—

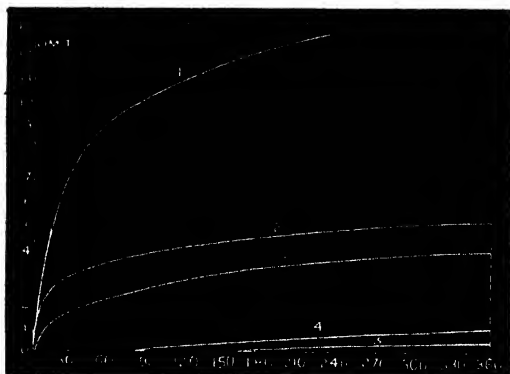
Time in minutes.	Reduction.	Mean curve values.		
		Oxidation.	Difference.	Oxygen added on per minute in each consecutive interval of time.
10	3·96	3·95	3·95	0·395
20	6·34	6·35	2·40	0·240
30	7·63	7·55	1·20	0·120
45	8·47	8·45	0·90	0·060
60	8·71	8·95	0·50	0·033
90	9·84	9·85	0·90	0·030
120	10·89	10·60	0·75	0·025
180	12·25	11·70	1·10	0·018
240	12·50	12·50	0·80	0·013

At 160° (turpentine vapour) and 130° (fusel oil) the following numbers were obtained:—

At 160°.		At 130°.	
Time in minutes.	Oxidation.	Time in minutes.	Oxidation.
15	0	15	0
30	0	60	0
45	0	180	0
60	0	210	0.03
120	0.18	270	0.31
180	0.48	480	0.31
240	0.79		
360	1.08		
530	1.66		
1005	2.20		
1320	2.21		

The curves marked 1, 2, 3, 4, and 5, Fig. 4, represent respectively these results obtained at 360°, 210°, 184.5°, 169°, and 130°; the obliquely vertical line marked "limit" represents the line that would be traced out were all the oxygen of the average air stream absorbed,

FIG. 4.



i.e., were 0.395 per cent. of oxygen continually added on per minute. In order to form Cu_2O an addition of 12.6 parts of oxygen per 100 of copper would be requisite, requiring nearly 32 minutes. This point was nearly reached in 240 minutes in the experiments at 360°.

On constructing a surface and taking sections the following values are obtained :—

Amounts of Oxidation produced in given Times at various Temperatures.

Time in minutes.	Oxidation.				
	130°.	160°.	184.5°.	210°.	360°.
5	0	0	0.60	1.80	1.97
10	0	0	0.90	2.42	3.95
15	0	0	1.12	2.70	5.45
20	0	0	1.30	2.90	6.35
30	0	0	1.57	3.20	7.55
45	0	0	1.90	3.45	8.45
60	0	0	2.18	3.60	8.95
90	0	0.06	2.64	3.85	9.85
120	0	0.18	2.96	4.06	10.60
150	0	0.33	3.20	4.25	11.20
180	0.03	0.48	3.39	4.42	11.70
240	0.10	0.78	3.65	4.75	12.50
360	0.31	1.08	3.85	5.25	—

Lengths of Time in Minutes requisite to produce given Amounts of Oxidation.

Oxidation.	Time.			
	At 160°.	At 184.5°.	At 210°.	At 360°.
1	344	12	3	3
2	—	51	7	5
3	—	125	23	7
		upwards of		
4	—	360	112	10
5	—	—	300	13
6	—	—	—	18
8	—	—	—	37
10	—	—	—	96
12	—	—	—	205

From the experiments detailed in Reports I to IV the following salient conclusions may be finally drawn, in addition to minor allied results of more or less interest referred to *passim*.

When a metallic oxide is acted upon by a reducing agent under constant conditions (or approximately so):—

(1.) In many cases the existence of "chemical induction" is traceable, *i.e.*, the action is at first slight or even *nil* (period of incubation), but commences after a longer or shorter time, and proceeds at an accelerating rate until other retarding influences (such as the mechanical or other action of the products of the reaction) cause the rate of reduction to cease increasing and subsequently to diminish again.

(2.) The period of incubation, when measurable, is shorter the higher the temperature. The rate of reduction attained to after any given time (before the retarding influences come markedly into play) is greater the higher the temperature, as is also the maximum rate attained.

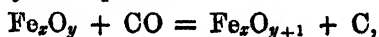
(3.) The oxides of metals (*e.g.*, copper) which develop sensibly the same amount of heat per given weight of oxygen combined with them no matter what oxide results, when deoxidised under constant conditions, are reduced at rates expressible by a curve of the general character that the earliest portion of the curve is concave upwards (whilst induction is going on), and the latter portion concave downwards (when the retarding influences come into play), so that a point of contrary flexure exists; but neither at this point nor anywhere else is there any abrupt alteration in the rate of reduction, *i.e.*, the curve exhibits no "angle."

(4.) The oxides of metals which develop more heat per given amount of oxygen combined in the formation of a lower oxide than in that of a higher one (*e.g.*, iron) give curves analogous to those yielded by copper oxide; with this difference, that at a point in the curve corresponding to the lower oxide an abrupt alteration in the rate of reduction is noticeable under suitable conditions, thus giving rise to an "angle" in the curve. In the case of iron such an angle exists for Fe_3O_4 but not for FeO ; in the case of manganese two angles appear to exist, one corresponding to Mn_3O_4 , one to MnO .

(5.) On comparing together the oxides of two metals the formation of which corresponds to different heat evolutions per given amount of oxygen combined, the actions of a given reducing agent (under conditions the same for each oxide) may be expressed by two curved surfaces, such that the surface corresponding to the oxide in the formation of which most heat is liberated, lies inside the other surface (*e.g.*, iron and copper).

(6.) On comparing together two reducing agents, the oxidation of which gives rise to different amounts of heat per given amount of oxygen consumed, the actions on these of a given metallic oxide (under conditions the same for each reducing agent) may be expressed by two curved surfaces, such that the surface corresponding to the reducing agent evolving the least heat during oxidation, lies inside the other surface (*e.g.*, hydrogen and carbon oxide).

(7.) A partial exception to this (as regards certain portions of the two surfaces) is noticeable when iron oxide is employed with hydrogen and CO as reducing agents, owing to the interference with the reducing action proper of carbon oxide of the tendency to a second reaction, indicated by the equation—



this second reaction being of an opposite character (*i.e.*, tending to re-oxidise the iron), and having no analogue when hydrogen is the reducing agent.

(8.) Another partial exception to this rule is noticeable when manganese dioxide is employed and hydrogen and CO are the reducing agents (probably also in other cases), owing to the unequal retardation in the rate of reduction produced by the formation of a film of partially reduced substance on the exterior of the particles of metallic oxide employed, the superior diffusive powers of hydrogen and steam over those of CO and CO₂ respectively causing the retardation to be markedly less in amount with hydrogen than with CO, so that after a certain lapse of time the total amount of reduction produced by the hydrogen under given conditions rises up to and then surpasses that produced by the CO.

(9.) The partial exceptions due to these (and possibly other) interfering causes being left out of consideration, the rule is always observed that in any two comparable cases of reduction, in the case of the reaction in which the heat evolution is algebraically the greatest, the length of time requisite to produce a given amount of reduction at a given temperature is less; the amount of reduction produced in a given time at a given temperature is greater, and the temperature requisite to produce a given amount of reduction in a given time is lower than in the case of the other reaction. A particular case of this general law is the rule arrived at in Reports I and II, that the greater the heat evolution in comparable cases the lower the temperature at which reduction first becomes manifest to a minute extent in a given period of time, *i.e.*, the lower is the "temperature of initial action."

LXXIII.—*Report on the Atmospheric Oxidation of Phosphorus and some Reactions of Ozone and Hydric Peroxide.*

By C. T. KINGZETT, F.I.C., F.C.S.

1. *Introductory.*

THE investigations of Schönbein, commencing in 1839, led him to believe that many processes of slow oxidation give rise to the formation of ozone. Among such processes investigated was the atmospheric oxidation of phosphorus in presence of water. The extent to which Schönbein proved that ozone is produced in this particular

case of slow oxidation, was narrowed by the fact that for many years subsequent to 1839, the true constitution of ozone was not decided. He was, therefore, unable to apply any absolutely decisive tests, although he observed that the active agent resembled ozone in its odour, and in its general chemical effects, so far as these were then recorded. He and others likewise supposed that ozone was produced by the slow oxidation of turpentine, ether, and other substances. My own investigations of the aerial oxidation of turpentine (*Chem. Soc. J.*, 1874, 511.; and 1875, 210; also *Chem. News*, **32**, 138; **34**, 127; and **39**, 279) have shown that ozone is not produced in the operation, but that peroxide of hydrogen results as a secondary product of the action of water upon a peroxidised derivative of turpentine.

Having regard to these results, and in view of certain other circumstances to be recorded hereafter, I was induced to re-open the question of the oxidation of phosphorus in a paper (*Chem. News*, **40**, 96), in which a number of facts were adduced which seemed to throw doubt upon the formation of ozone. These facts may be briefly recited as follows:—

(a.) M. Corne (*Journ. de Pharm.* [4], **22**, 425) observed that the water in which phosphorus has undergone spontaneous oxidation liberates iodine from iodates and iodides of the metals, a reaction which would characterise peroxide of hydrogen if present, and not phosphorus acid as assumed by the author of the paper in question.

(b.) Andrews has also placed upon record (*Phil. Trans.*, 1856, 1) the observation that air rendered active by passing it over moist phosphorus, loses its properties when agitated with water, a result which seemed to be due to the solution of suspended vesicular peroxide of hydrogen in water.

(c.) Marignac demonstrated the necessity of the presence of water in the process under consideration, in order to obtain an active aerial product, and this also seemed to me to point to the formation of peroxide of hydrogen rather than to that of ozone.

(d.) D. J. Boehe (*Ber.*, **6**, 439) states as the result of his own experiments, that peroxide of hydrogen is produced in the process.

(e.) The products of the oxidation of phosphorus have been tested by the several chemists concerned, in such ways as not to preclude the possibility of the active agent being peroxide of hydrogen.

Before the subject was thus re-opened, Dr. A. R. Leeds had described a number of interesting experiments (*Chem. News*, **39**, 157; and **40**, 70) upon the oxidation of phosphorus, and had shown that so far as the active substance which is eventually obtained in the aerial current is concerned, it is increased by substituting a mixed solution of potassic dichromate and dilute sulphuric acid for water

only. But such a method of experiment obviously precluded examination for peroxide of hydrogen* in this solution in which the phosphorus was partially submerged. Moreover, it is not apparent from his various communications, that he subjected his gaseous product to any very special examination. He seems to have relied upon its odour and general characters rather than upon any exclusive properties, as evidence of its nature.

Schönbein was of opinion that peroxide of hydrogen in very small amount accompanies ozone†, as produced by the oxidation of phosphorus, and Dr. Leeds in the course of his investigation, tested for this substance in the wash-water through which the gas had passed, and obtained evidence of its presence there in very small quantity. I shall show hereafter that he overlooked the bulk of it, which is to be found in the oxidisers themselves, and not in the wash-water. In a later communication (written partly in answer to my paper above referred to) Dr. Leeds says (*Chem. News*, 41, 164), "In the oxidation of phosphorus in moist air there are formed both *ozone and hydrogen peroxide*. The amounts of the two bodies evolved, under given circumstances, bear a constant relation to one another, and to the air passed over, the percentage of hydrogen peroxide being very small, as compared with that of the ozone. In the experiments quoted above, the temperature being 18° to 21° C., the percentage of ozone, as referred to the weight of air aspirated, was 0.15 per cent., that of hydrogen peroxide was 0.00038 per cent., or but 1.400th part of the ozone."

Subsequently to the publication of my earlier paper, Prof. H. McLeod made some experiments (*Chem. Soc. J.*, 37, 118) upon this subject. He conducted his investigation upon the view that "the active substance formed during the slow oxidation of phosphorus is probably either ozone or peroxide of hydrogen," "for (he writes) the bodies decompose one another under certain conditions." His method consisted in exposing the gas to conditions which would presumably destroy any peroxide of hydrogen that might be present without affecting ozone, and operating thus, he came to the conclusion that the only product is ozone. The experiments were chiefly of a qualitative nature; they were calculated rather to destroy peroxide of hydrogen than to discover it, and they only established the formation of ozone in quite a negative way.

As these results did not appear to be quite so decisive and comprehensive as could be wished, I determined to make a further investi-

* Explaining why he found the relation of peroxide of hydrogen to ozone as 1 : 400!

† But neither he nor Dr. Leeds supposed that peroxide of hydrogen was produced in such amount as to constitute one of the chief products.

gation, which I now beg to describe to the Society, merely remarking in advance that the main results were communicated verbally and in abstract to the Chemical Society, on June 3rd, 1880 (*Chem. News*, **41**, 269; and **42**, 34), and that I have been assisted in carrying out the inquiry by a grant from its Research Fund.

2. *The Oxidation of Phosphorus.*

The apparatus used in my experiments was specially constructed for the purpose, and consisted of a number of wide-mouthed bottles, each of 300 c.c. capacity, and having well-fitting solid stoppers, provided with two apertures. Through these apertures with ground surfaces there passed tubes, enlarged and ground at the requisite positions, so that when they were fitted into their proper places, the joints were perfectly tight, and easily disconnected or renewed. This special form of apparatus was adopted in order to avoid the contact of oxidisable materials in the construction of joints, and it is apparent that a perfect battery of such oxidisers could be used, the tubes of the various members being connected in the manner described by Sir Benjamin Brodie, by means of paraffin, &c.

In each of five such oxidisers was placed a stick of phosphorus, scraped clean just before use, and then sufficient water to half submerge the phosphorus, leaving the other half entirely exposed to the air in the bottles. The sixth vessel was charged with 200 c.c. water, to serve as a wash-bottle, and then the series was connected together, and a current of air previously filtered through cotton-wool and washed in water, was in each experiment blown through by means of a rotating fan.

In the earlier experiments, which were conducted in the month of February, 1880, and in a cold room, I obtained no satisfactory evidence of the formation of ozone, and but little evidence of the production of peroxide of hydrogen; but this seems to have been caused by the low temperatures. In his paper previously referred to, I find that Dr. Leeds has recorded a similar observation, and he fixes the best temperature to employ at 24–25° C. I think these facts sufficiently important to instance, as the record may save others from obtaining unsatisfactory results with the process.

Experiment 1.—Through the apparatus already described a current of air was blown at the rate of 3 to 4 litres per hour for two hours, and the washed gas was passed through an acidified solution of potassium iodide. In this way the amount of iodine set free in the Liebig bulb required only 0.8 c.c. of a decinormal solution of sodium thiosulphate. The wash-water gave the faintest reaction with potassium

iodide and starch, but the water in which the phosphorus was placed gave iodine, requiring 2.2 c.c. thiosulphate.*

Experiment 2.—In another experiment each oxidiser was charged with a clean stick of phosphorus, and 30 c.c. pure water. Between the potassium iodide bulb and the wash-bottle a sulphuric acid tube (charged just as in an organic combustion) was interposed, the cork being well coated with melted paraffin, and inserted whilst hot. Two potassium iodide bulbs were then attached, but the reagent was not acidified in this case, because it has been shown that the passage of air alone through acidified KI in daylight liberates some iodine. The strength of the KI was 10 per cent. The air-current varying from 3 to 6 litres per hour was kept up for three hours, but still no iodine was liberated in the Liebig's bulbs, except as much as required two drops of thiosulphate. The water in which the phosphorus was oxidised liberated iodine from KI = 1.6 c.c. N/10 thiosulphate. Subsequent experiments showed, as already stated, that the foregoing negative results (as regards ozone) were obtained by working at too low a temperature.

Experiment 3.—In this case the method of proceeding was the same in all respects as in Experiment 2, except that the experiment was performed in summer weather, the air-current being from 4 to 7 litres per hour. Iodine was gradually set free in the potassium iodide contained in the first bulb, the second bulb being found unnecessary. At the end of one hour the iodine liberated required 2 c.c. N/10 thiosulphate. The gas which thus liberated iodine was found to smell strongly, like ozone; it rapidly corroded, and made its way through india-rubber; gave no reaction when passed into a dilute solution of potassium dichromate and sulphuric acid, and exhibited powerful bleaching characters; for instance, it rapidly discharged the colour of copying ink from a piece of linen steeped in the fluid.

Experiment 4.—In this experiment, conducted under the same other conditions as Experiment 3, the first bulb of 10 per cent. solution of potassium iodide was removed and substituted for one containing Russian oil of turpentine. The air-current remained the same, and although it was kept going for one hour, no iodine was set free in the KI solution; in other words, the turpentine totally absorbed the active agent.

Experiment 5.—Here again two bulbs of potassium iodide were employed, and the solution was acidified with dilute sulphuric acid. During one hour there was liberated in the first bulb iodine equal to 5.4 c.c. N/10 hypo-, but in the second bulb the iodine set free required only two drops of the standard thiosulphate. The iodine set free in

* See *Chem. News*, 41, 182, where an account of this preliminary experiment is recorded.

the second bulb may be regarded as the measure of the action of ordinary air upon acidified potassic iodide in this particular experiment.

Experiment 6.—Having now ascertained in Experiment 5 the rate of formation of ozone under the then existing conditions, a coiled tube was interposed between the sulphuric acid tube and the acidified potassium iodide bulb (in which of course the solution was renewed). The coiled tube was maintained at about 240° , and the air current kept up during one hour. At the end of that time it was observed that no iodine had been set free above the quantity which the air current alone accounted for, and which required only two drops of the standard thiosulphate. Thus it was proved that a temperature of 240° decomposes the active agent. To corroborate this fact, the coil was allowed to cool, and the experiment being continued for another hour, iodine was then liberated = to 6 c.c. thiosulphate.

Experiment 7.—After the apparatus had been in use for several experiments, the water contained in the five oxidisers was mixed, strongly acidified with dilute sulphuric acid, and an excess of potassium iodide added. Iodine was at once liberated, and required a total of 10 c.c. standard thiosulphate.

Against this quantity, the water contained in the wash-bottle (200 c.c.) similarly liberated iodine = to 0.4 c.c. thiosulphate, showing that the active agent present in the water in which the phosphorus was oxidised was peroxide of hydrogen; for if it were ozone, we should expect to find much more in the wash-water through which all the gas passed than in the water contained in the oxidisers.

Experiment 8.—The apparatus was put together again as before, all reagents and solutions being renewed. But between the wash-bottle and the sulphuric acid tube, a bulb containing a solution of peroxide of hydrogen (10-volume strength) was interposed. The sulphuric acid tube was followed by a bulb containing acidified 10 per cent. solution of potassium iodide. During one hour the current of gas liberated iodine = to 4 c.c. standard thiosulphate. This experiment shows that by passing very dilute ozone through a solution of 10-volume peroxide of hydrogen, it is not materially, if at all, decomposed.*

Experiment 9.—In this case the H_2O_2 bulb was removed, and the active gas passed alone into the acidified potassium iodide solution during three hours. At the end of that time the free iodine required 24 c.c. thiosulphate.

The water in the wash-bottle had been the same in Experiments 8 and 9, and had therefore been exposed to the current of active gas

* It was specially proved that when a current of air is rapidly passed through a 10-volume solution of H_2O_2 no peroxide is carried over with the current.

during four hours; it gave on treatment with acidified potassium iodide, iodine requiring only 0.6 c.c. thiosulphate.

The united water from the five oxidisers (145 c.c.) contained peroxide of hydrogen = to a total of 11.6 c.c. thiosulphate. This was proved by taking a measured part, adding excess of dilute H_2SO_4 and KI, and determining the iodine set free: thus 20 c.c. required 1.6 c.c. thiosulphate. Another quantity of 20 c.c. gave a visible reaction with acidified potassium dichromate, characteristic of peroxide of hydrogen. Further, 105 c.c. were evaporated in a glass dish on a water-bath.

After 5 minutes' evaporation, 10 c.c. = 0.8 c.c. standard thiosulphate solution.

After 15 minutes' evaporation, 10 c.c. = 1.0 c.c. standard thiosulphate solution.

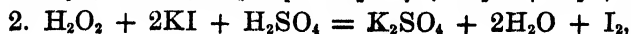
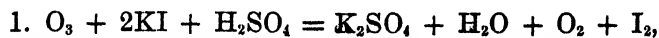
After 30 minutes' evaporation, 10 c.c. = 1.8 c.c. standard thiosulphate solution.

After 50 minutes' evaporation, the last 10 c.c. = 3.6 c.c. standard thiosulphate solution.

Thus, the active constituent, instead of being speedily expelled by the heat as ozone would be*, was actually and largely concentrated. Moreover, it possessed the bleaching and other effects of peroxide of hydrogen, which substance it undoubtedly was.

Experiments 8 and 9, being successive, and lasting four hours altogether, furnish a very good opportunity of calculating the relative proportion of ozone and peroxide of hydrogen obtained, as also the percentage of both these substances in reference to the volume of air employed. The total quantity of ozone produced was equal to 28 c.c. N/10 thiosulphate. The total peroxide of hydrogen, to 11.6 c.c. of the same reagent.

Using the two equations—



we arrive at the result that the total quantity of ozone amounted to 0.0672 gram, and the peroxide of hydrogen to 0.0197 gram. Taking the peroxide of hydrogen to be correctly ascertained, then this substance and ozone were obtained as nearly as possible in the relation of 1 : 2.4 (molecules)†. Assuming the total air employed to be 24 litres, then this would weigh 30.926 grams; the percentage of ozone pro-

* Assuming a solubility which it does not exhibit.

† The figure for ozone would be a little too high, on account of the action of air upon acidified KI in daylight.

duced would be 0.217, and the percentage of peroxide of hydrogen, 0.063.

In another experiment, the details of which it is not necessary to give, the peroxide of hydrogen solution was also concentrated and then treated with excess of potassium permanganate, when oxygen gas was obtained in measurable quantity. I submit, therefore, that the foregoing experiments prove that both ozone and peroxide of hydrogen are produced by the passage of air over phosphorus partly submerged in water. The ozone is totally absorbed by oil of turpentine, and is entirely destroyed by a temperature of 240° ; it is not materially, if at all, decomposed by passing through a strong solution of hydric peroxide. The peroxide of hydrogen is formed in the oxidisers, where it at once dissolves in the water, and does not pass on with the current of gas. As regards the precise relative proportions of ozone and peroxide of hydrogen, this is a matter demanding more delicate apparatus and a longer time than are at my present disposal.

While I was conducting the experiments here detailed, Dr. Leeds was, unknown to me, also occupied with a similar study, and almost at the same time announced his results; so that, whereas I gave a brief description of my results at the meeting of the Chemical Society on 3rd June, 1880, Dr. Leeds' paper (*Chem. News*, **42**, 17) was published on June 14th.

I have already pointed out that Dr. Leeds, in his original investigation, determined the peroxide of hydrogen upon "the assumption that it is completely absorbed by the washing water," and thus he found its proportion to the ozone to amount to $\frac{1}{410}$. However, in his most recent paper referred to above and communicated to the Berlin Chemical Society, he abandons this view, although he still ignores the deposition of the peroxide in the oxidisers themselves. He now assumes that the peroxide of hydrogen escapes out of the oxidisers and fails to be washed out by passing through five successive bottles of water, an empty bottle, a bottle containing strong sulphuric acid, and sulphuric acid drying tubes of 2.5 metres length packed with glass beads moistened with the acid, but is at last decomposed on heating the current of gas to various elevated temperatures; "the quantity of water thus found increases regularly, till at 200° all the hydrogen peroxide is transformed into water" (see *Chem. News*, **42**, 19). This water is of course weighed. Its amount varied in his experiments from .0002 to .0018 gram (maximum).

In my opinion, chemists cannot attach much significance to such figures; and moreover, on careful examination of Dr. Leeds' results, it will be seen that in one case exposure of the gas to 100° produced .0002 gram of water, whereas in other two cases he obtained .0015, and at 200° in two cases only .0010 and .0011 respectively; while in yet

other cases a corresponding amount of water as in these last-named instances was obtained at 50°.

I do not hesitate to state my conviction that, no matter how much water was obtained in Dr. Leeds' determinations, it was obtained from water only, and not by the decomposition of peroxide of hydrogen. This is confirmed by the fact, that in all his twelve experiments he only obtained a total of .00029 gram H_2O_2 in all the washing water.

Against his conclusions then, I may summarise as follows:—

1. The peroxide of hydrogen formed in the process is entirely deposited in the water contained in the oxidisers; and if it cannot escape condensation in the aqueous spray and vapour of the oxidisers, it cannot be expected to escape solution in five wash-bottles.

2. Neither Dr. Leeds nor myself find any appreciable quantity of peroxide of hydrogen in the wash-water.

3. I have proved by experiment that the spray of peroxide of hydrogen cannot be carried so far suspended in air as Dr. Leeds would make out. For instance, during half-an-hour a rapid current of air was passed through a 100 c.c. of a 10-volume solution of H_2O_2 into a Liebig's bulb containing acidified potassium iodide. The iodine set free required two drops only of a N/10 thiosulphate solution, and when a water wash-bottle was interposed between the peroxide and the iodide, no iodine at all was liberated.

3. *The Action of Ozone upon Turpentine, &c.*

To Soret we owe the original observation, that the whole molecule of ozone is absorbed by oil of turpentine; but until recently there was no explanation of this fact forthcoming. In my examination of the atmospheric oxidation of terpenes, I showed that oxygen is first absorbed and gives rise to the production of a peroxidised product, which afterwards forms peroxide of hydrogen on treatment with water; and in March, 1875 (*Chem. Soc. J.*, Series 2, 13, 210), I explained the absorption of ozone by turpentine in the same way. But it is only quite recently that I have been afforded the opportunity of placing this explanation upon an experimental basis. Turpentine which had been used to absorb the ozone produced by oxidising phosphorus was examined, and found to give rise to peroxide of hydrogen when placed in contact with water, just as the oxidised oil does which is obtained by blowing air through hot turpentine. This may be instanced by the following special experiment:—An ozonised current of air obtained in the manner already described and washed in water was passed through a Liebig's bulb charged with Russian turpentine during four hours. After that time the products were allowed to stand

overnight, and were examined next morning. The water from the five oxidisers holding the phosphorus proved to contain peroxide of hydrogen = to 10·6 c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3$ solution. The water in which the gas was washed liberated only sufficient iodine from acidified potassium iodide to require 0·5 c.c. thiosulphate. The oil of turpentine was originally of a pale yellow colour; but after the experiment it was quite colourless, and differed from the original oil in rapidly decomposing acidified potassium iodide. Experimenting with a portion of this product, it appeared that the total oxidising power was equivalent to about 14 c.c. N/10 thiosulphate. A measured portion of the oxidised oil was agitated with water and left in contact therewith for about ten minutes. Calculating from the result of the examination of this aqueous product, it appeared that the whole of the oxidised oil was capable of producing such an amount of peroxide of hydrogen as would correspond approximately to the total oxidising power of the oxidised oil itself (20 c.c. of the aqueous solution produced required 3·4 c.c. N/10 thiosulphate). The aqueous solution formed by treating the oxidised oil with water exhibits all the characters and properties of a dilute solution of peroxide of hydrogen. Oxygen gas may be obtained from it, and estimations giving concordant results were made by the potassic iodide and the permanganate methods.

A check experiment was carried out by passing a current of pure air, washed in water, through oil of turpentine exactly as in the manner described. The air-current was maintained for four hours, but the intermediate peroxide produced was only equivalent (in terms of peroxide of hydrogen) to less than 1 c.c. of the N/10 thiosulphate. As I have elsewhere pointed out, air requires an elevated temperature to oxidise turpentine to any considerable extent.

Thus it is seen that by the action of ozone upon turpentine a body is produced which (like that which obtains when air is substituted for ozone) yields H_2O_2 on treatment with water.

In connection with this subject, the oxidation of ethylic ether presents many points of considerable interest. This oxidation is generally supposed to be accompanied by the formation of ozone, but in some experiments which I conducted some years since (*Chem. News*, **34**, 127), although ozone was not detected, a plentiful formation of peroxide of hydrogen was observed, and I attempted to explain its production by the direct formation of an intermediate body which afterwards yields peroxide of hydrogen when treated with water.

Some recent investigations conducted by M. Berthelot (*Compt. rend.*, **86**, 71—76; *Chem. Soc. J.*, May, 1878, 372), have given additional force to this explanation. He has shown that ozone may be changed, so to say, into peroxide of hydrogen by the intervention of ether, an intermediate body being formed, which he calls "ozonised

ether," and this, when shaken with water, produces peroxide of hydrogen.

Under these circumstances it becomes even more interesting to work out the true explanation of the facts associated with the atmospheric oxidation of phosphorus. Is ozone directly produced in the manner supposed by Lamont (*Chem. News*, **28**, 236), by a splitting up of molecular oxygen, and does a part of the ozone then combine with the phosphorus to form a peroxidised substance which then gives rise to peroxide of hydrogen by contact with water? Or are ozone and peroxide of hydrogen both directly and simultaneously formed in some way? Or are they both secondary products? These are questions yet to be settled, but it seems probable that there is some near degree of similarity in the manner in which, at any rate, peroxide of hydrogen is produced in the three processes of direct oxidation of turpentine, ether, and phosphorus.

4. *The Estimation of Peroxide of Hydrogen.*

It is well known to chemists that, when a dilute solution of peroxide of hydrogen is faintly acidulated and placed in contact with a solution of potassium iodide, a certain amount of iodine is at once liberated, but a long time (in certain cases many hours) is requisite for the peroxide of hydrogen to perform its full power of oxidation.

Harcourt and Esson, in their well-known study of this reaction, showed that the amount of change in a given time varies directly (1) with the amount of iodide present; (2) with the amount of peroxide; (3) with the total volume of the solution; and (4) with some function of each of the other conditions under which the change occurs.

Under ordinary circumstances, indeed, this process of determining peroxide of hydrogen is so slow as to be prohibitory of its employment when it is constantly required to make a large number of analyses. But I have found, in course of a great deal of experience with this subject, that the method may be so worked as to occupy a very little time, thus obviating the difficulty in question. This modification consists in the employment of a very great excess of sulphuric acid, instead of being content with mere acidity, and it will be seen to constitute an important consideration in any question regarding the chemical system of change studied by Harcourt and Esson. To illustrate the process.

Experiment 1.—A dilute solution of peroxide of hydrogen was first demonstrated to contain such an amount of H_2O_2 in 10 c.c. as is competent to liberate iodine under the most favourable circumstances, requiring 6.2 to 6.3 c.c. $\text{N}/10 \text{ Na}_2\text{S}_2\text{O}_3$. Six portions of the solution

of peroxide (A, B, C, D, E, F) of 10 c.c. each were placed in separate glasses. To A no acid was added, but to the solutions B, C, D, E, F were added respectively 5, 10, 20, 30, and 50 c.c. of 1 : 3 sulphuric acid. To each solution was now added sufficient potassic iodide in crystals, and a little starch. After an interval of five minutes, the iodine liberated in each glass was estimated by titration with the standard thiosulphate.

A required 1·8 c.c. $\text{Na}_2\text{S}_2\text{O}_3$.

B " 6·1 " "

C " 6·2 " "

D " 6·2 " "

E " 6·3 " "

F " 6·3 " "

The colour of A did not subsequently return as it does in cases where a very little acid is present, and, consequently, where the oxidation proceeds but slowly. After half an hour further, 10 c.c. of the acid was added to A, and this brought back the blue colour which took another 1·3 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ to remove. The colour did not return again. Now $1·8 + 1·3 =$ a total of 4·1 c.c., against 6·2—6·3 in the other cases, showing a loss of oxygen in some way.

Among the other cases, in B only did the colour come back, and this it took only 0·3 c.c. thiosulphate to remove. In other words, in the cases where an abundant excess of acid was present, the decomposition of the hydriodic acid, $2\text{HI} + \text{H}_2\text{O}_2 = 2\text{H}_2\text{O} + \text{I}_2$, was completed in a very brief space of time.

Experiment 2.—Again, another solution of peroxide of hydrogen was prepared and two portions of 10 c.c. taken.

A was treated with KI and starch without acid.

B was first treated with 10 c.c. 1 : 3 H_2SO_4 .

After five minutes—

A required 0·4 c.c. $\text{Na}_2\text{S}_2\text{O}_3$.

B " 7·2 " "

In B the decomposition was already complete.

In A the colour did not return after standing thirty minutes longer.

Then 10 c.c. of the acid was added; this restored the colour, and the mixture now required 0·7 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ to decolorise it.

Now $0·4 + 0·7 =$ only 1·1 c.c. $\text{Na}_2\text{S}_2\text{O}_3$, showing again, in the case of the peroxide which had been in contact with potassic iodide alone, a great loss of oxygen.

Before proceeding further, I may state that I have performed many hundred determinations of peroxide of hydrogen (from the most dilute solution up to those of about 5-volume strength) with this modified process with accuracy and with great expedition.

The following experiments were intended to explain the other circumstances above referred to.

Experiment 3.—A new solution of peroxide of hydrogen was taken. 20 c.c. + 10 c.c. acid liberated iodine from KI = to 13.4 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ in five minutes.

20 c.c. + 1 c.c. acid liberated in the same time—

Iodine equal to	7.2 c.c. $\text{Na}_2\text{S}_2\text{O}_3$.
After an interval	2.8 „ more was required.
After a second interval.....	1.6 „ further „
After a third interval	1.0 „ „ „
<hr/>	
Total	12.6

This result is below the full value of the peroxide of hydrogen employed, although it does not exhibit the enormous loss of oxidising power which is experienced in the total absence of acid.

Experiment 4.—The peroxide of hydrogen employed was acid in itself; in one case from sulphuric acid and in the other case from acetic acid, both derived from the two methods of manufacture; and it occurred to me that if this acidity were neutralised peroxide of hydrogen would not liberate iodine from potassium iodide at all. A solution of peroxide (acid to test-paper) was now made, of which 20 c.c. was known to exercise a total oxidising power = 14 c.c. $\text{Na}_2\text{S}_2\text{O}_3$. A second quantity of 20 c.c. liberated from KI, iodine = 1.2 c.c. $\text{Na}_2\text{S}_2\text{O}_3$, in five minutes and the colour did not return. The mixture was now observed to be faintly alkaline, and minute bubbles of gas were being evolved. After half an hour further 10 c.c. of 1 : 3 H_2SO_4 was added, and this gave more iodine, requiring a further 1 c.c. $\text{Na}_2\text{S}_2\text{O}_3$.

Experiment 5.—Some of the peroxide solution (of which 20 c.c. = c.c. 14 c.c. $\text{Na}_2\text{S}_2\text{O}_3$) was now neutralised with pure caustic soda, and to 20 c.c. of this solution was added KI and starch as usual; a trace only of iodine was set free, and bubbles of oxygen. After two minutes 10 c.c. acid was added, and this liberated iodine = to 9 c.c. $\text{Na}_2\text{S}_2\text{O}_3$, so that during the small period of two minutes peroxide of hydrogen = 5 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ had suffered decomposition without liberation of iodine.

Experiment 6.—5 c.c. of a 10-volume solution of hydric peroxide was diluted to 100 c.c. and the solution as nearly as possible neutralised. Iodine was set free on the addition of KI equal to only 1.8 c.c. N/10 thiosulphate solution, and at the same time the solution became alkaline to test paper and evolved oxygen. After 30 minutes the solution was acidified with 10 c.c. 1 : 3 H_2SO_4 , but the iodine now set free required only 0.2 c.c. of the standard thiosulphate.

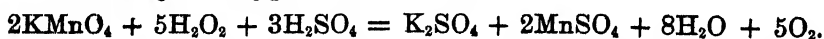
From these observations it is to be concluded that :—

- (1.) Pure neutral peroxide of hydrogen does not decompose potassium iodide with liberation of iodine although it undergoes spontaneous decomposition.*
- (2.) Ordinary peroxide of hydrogen liberates a little iodine from potassium iodide, because of its acidity (impurity).
- (3.) In contact with pure KI, pure peroxide of hydrogen undergoes rapid decomposition into water and oxygen.
- (4.) Peroxide of hydrogen is most conveniently and accurately estimated by the use of potassium iodide in presence of a great excess of dilute sulphuric acid.

The precise function played by the excess of sulphuric acid is not easy to imagine, but it is not impossible that the change may be related in some way to the fact observed by Berthelot (*Compt. rend.*, **86**, 71—76; *Chem. Soc. J.*, 1878, **34**, 372) that hydric peroxide combines with *strong* sulphuric acid to form per sulphuric acid, which is a body of great oxidising powers and which readily parts with all its oxygen.

5. Determination of Hydrogen Peroxide with Potassium Permanganate.

Another method often employed in the determination of peroxide of hydrogen consists in mixing the solution to be examined with excess of potassium permanganate acidulated with dilute sulphuric acid and measuring the oxygen evolved, thus :—



In this reaction half the oxygen evolved is derived from the peroxide and half from the permanganate. In my earlier experiments I often employed this method and found it to give results fairly concordant with those obtained by the hydriodic acid method;† but more recently I have experienced a source of danger which it may be well to point out.

I have usually employed a burette (containing the peroxide) which terminates in a small Wolff's bottle by means of an india-rubber cork, the Wolff's bottle being charged with the mixture of potassium permanganate and sulphuric acid, and being provided at the other neck with a bent delivery tube for conducting the gas for collection in a measured tube over water.

* E. Schöne (*Liebig's Annalen*, 195; *Chem. Soc. J.*, 1879, **36**, 353) has already noticed that hydrogen peroxide in contact with pure potassium iodide liberates oxygen and becomes alkaline; but although he regards the action as catalytic, the KI being constantly decomposed and regenerated, he yet states that iodine is *liberated*. This seems to me an inconsistency, and I cannot understand how he can advocate the use of this system of changes for determining atmospheric H_2O_2 . (See also *Zeits. Anal. Chem.*, 1879, 183—158; *Chem. Soc. J.*, 1879, **36**, 740.)

† See, for instance, *Chem. Soc. J.*, **28**, 210.

Experiment 1.—On one occasion, wishing to check the determination of H_2O_2 in the fluid (resulting from the oxidation of turpentine over water) as obtained by the hydriodic method, by means of the permanganate method, I used the arrangement just described.

By the HI method 100 c.c. of the fluid required 60 c.c. $\text{Na}_2\text{S}_2\text{O}_3$, of which 1 c.c. = 0.01134 gram iodine = 30 c.c. of oxygen. 50 c.c. of the peroxide solution was run from the burette into the Wolff's bottle and the latter then agitated. Gas was at once evolved and was collected over water, but not only was the gas evolved at the time, but it continued to be steadily evolved during the next 24 hours. It then measured 160 c.c. Now 160 c.c., less 50 c.c. (being measure of peroxide solution used) = 110 c.c., half of which by the method is supposed to come from the peroxide, so that 100 c.c. of the fluid, instead of giving only 30 c.c. oxygen from itself, gave 110 c.c.

In order to ascertain whether this result was brought about by any other constituent of the mixture than peroxide of hydrogen, fresh amounts of permanganate and dilute (1 : 3) H_2SO_4 were placed together in the Wolff's bottle without anything else. For a few minutes no gas was evolved, but after a time gas passed over, and between 4 P.M. of that day and 12 A.M. of the next there was collected 90 c.c. of oxygen in this way. During the next 48 hours a further 100 c.c. of oxygen was collected, and gas continued to be evolved during about 30 days, much oxide of manganese being deposited, and the colour of the solution finally disappearing simultaneously with the evolution of oxygen.

I have repeated this experiment with various specimens of permanganate and have always obtained similar results, but whether it is due to any impurity, or to what cause, I have not had full opportunity of deciding. This evolution of oxygen will last during some weeks, until in fact there is no free acid left, or until all the permanganate is decomposed, according as to which substance is present in excess. But with the fact before us, it is serviceable as a warning to those chemists who would employ this method for the determination of hydric peroxide and interesting in itself.

Experiment 2.—While at this subject I examined the method of using KMnO_4 evolution *without acid*.

20 c.c. of the peroxide solution run in as usual gave off 33 c.c. gas. $33 - 20$ (volume of air displaced by the fluid) = 13 c.c., and this divided by 2 = 6.5, as the measure of oxygen from the hydric peroxide, or 32.5 c.c. oxygen from 100 c.c.; a result which, when corrected for temperature and pressure, fairly agreed with the result of the hydriodic method detailed above.

Again, 10 c.c. of a peroxide solution gave similarly as the result of a determination conducted by the KMnO_4 (without acid) method,

that it would evolve 50 c.c. gas from 100 c.c. fluid. By the hydriodic method 100 c.c. required 90 c.c. N/10 $\text{Na}_2\text{S}_2\text{O}_3$, which well agrees with the foregoing result.

A final corroboration of the concordant results obtained by the different processes may be here given.

By the hydriodic method 100 c.c. of a fluid showed that it should yield by the decomposition $\text{H}_2\text{O}_2 = \text{H}_2\text{O} + \text{O}$, 107 c.c. gas at 0°C . and 760 mm. B.

By the KMnO method (*without acid*) it gave 107 c.c. gas.

By the neutral bichromate method it gave 108 c.c. gas.

Again, a dilute solution of peroxide of hydrogen, obtained by the atmospheric oxidation of turpentine in the presence of water, showed by the hydriodic process that 100 c.c. required 160 c.c. $\text{Na}_2\text{S}_2\text{O}_3$ N/10 solution. This would indicate the presence of 0.272 gram H_2O_2 .

5 c.c. of the same solution gave by the KMnO_4 method (*without acid*) 13.9 c.c. gas. Now $13.9 \text{ less } 5 = 8.9$, and this $\div 2 = 4.45$ c.c. oxygen from the $\text{H}_2\text{O}_2 =$ to the presence of 0.2704 gram H_2O_2 per 100 c.c.

LXXIV.—On the Basic Sulphates of Iron.

By SPENCER UMFREVILLE PICKERING, B.A., Brackenbury Scholar of Balliol College, Oxford.

IN an investigation which the author of this present paper is now pursuing, the object of which is to throw some light on the constitution of basic salts, it was found necessary to obtain several different basic salts of some pseudo-tetrad metal combined with some dibasic acid. The basic persulphates of iron were selected as being the most promising, since, according to the literature on the subject, no less than fifteen of these bodies had been identified. With a view to confirming the somewhat shaky foundations on which the identity of most of these sulphates rested, as well as to prepare samples of any which could be obtained in a definite and stable form, the work detailed in the following pages was performed; and it is to be feared that the account of it will not be rendered less tedious and uninteresting than might be expected from the conclusions arrived at being almost entirely of a negative character, only one out of the fifteen above-mentioned sulphates having been proved to be a definite body.

I. Preparation of the Ferric Sulphate used.

A considerable quantity of normal ferric sulphate was prepared by

the usual method of oxidising ferrous sulphate by means of nitric acid; the persalt thus obtained, after being dried and powdered, was heated in an iron dish in small quantities at a time till it assumed a light brown colour while hot, becoming pink on cooling, which pink colour was due to the presence of free ferric oxide. This partial decomposition of the sulphate (which requires a low red heat) was found necessary to insure its perfect freedom from excess of sulphuric acid. The impalpable powder* thus obtained was mixed with about four times its weight of water, on which, if the quantities used are large, the heat developed is sufficient to effect its perfect solution; whereas if small quantities are operated on, the heat at first evolved is quickly dissipated, and the solution does not become complete till after many days.

The 20 per cent. solution thus obtained was found after filtration to possess a density of 1.208 at 15° C. A determination of the relative amounts of ferric oxide and sulphuric anhydride present gave—

	Found.	Theory.
Fe_2O_3	40.114	40.00
SO_3	59.886	60.00

showing that neither acid nor base were in excess.

— The solution possesses a deep brown colour, quite opaque in layers three or four inches thick, which colour is due to the partial decomposition of the sulphate by water, forming either a soluble basic sulphate or, more probably, some of Graham's soluble ferric oxide and a corresponding amount of free sulphuric acid.

II. *Dilution with Cold Water.*

When a solution of ferric sulphate is diluted with a large quantity of cold distilled water, the decomposing action of the water causes a larger amount of the soluble ferric oxide to be liberated, and this, combining with some of the still undecomposed sulphate, produces a cloudiness or precipitate of a basic sulphate. Time, however, is an important factor in this action; a solution, for instance, containing 0.0332 per cent. of the normal sulphate remaining perfectly clear for more than an hour.

A few experiments performed in this manner gave the following results:—

* In order that this powder should be impalpable and easily dissolved by water, the dry powdered salt, which still contains a small excess of sulphuric acid, should be heated as suddenly as possible to a temperature little short of redness.

TABLE I.—5 c.c. of Ferric Sulphate diluted with Various Amounts of Cold Distilled Water.

Amount of water added.	Percentage strength of solution produced.	Amount of precipitate obtained.	Percentage of Fe_2O_3 in the anhydrous precipitate.
1. 2,000 c.c.	0·058	0·2060 gram.	80·69
2. 3,500 "	0·0332	0·2732 "	80·91
3. 6,000 "	0·0203	0·3931 "	81·76

Five days were allowed to elapse in each case before the precipitate was collected and analysed.

The temperature varied between 13° and 18° C.

In the above table the data in the first column do not appear in strict accordance with those in the second column, the reason being that the strong ferric sulphate solutions used did not always possess exactly the same strength; the percentage of sulphate contained in them only varied, however, between 19·376 and 20·332.

The numbers given in the third column show that the basic sulphate precipitated corresponds very nearly to that represented by the formula $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, containing 80 per cent. of Fe_2O_3 , but that an excess of ferric oxide is always present, this excess increasing with the dilution.

In the earlier part of this work the precipitates were dried in an air-bath at 100° , and then, after being weighed, the ferric oxide and sulphuric oxide were both determined gravimetrically; as, however, the considerable amount of water combined with these basic sulphates was found to vary greatly with their composition and to give no aid in determining whether they were definite bodies or not, the operation of drying and weighing them was soon dispensed with, and the amount of the precipitate analysed taken as being the sum of the weights of Fe_2O_3 and SO_3 found. The numbers, therefore, which are given in the tables invariably refer to an anhydrous substance.

A great amount of accuracy was found impossible in analysing these basic sulphates, from the fact that they are more or less decomposed on being washed with cold water; this decomposition, however, proceeds very slowly, even with precipitates which have been obtained as those above described, without the application of heat, and still more slowly in cases where heat has been employed. A precipitate which had been obtained in the cold, and which, after having been washed about twenty times, was found to contain 80 per cent. of ferric oxide, was then washed in a continuous stream of cold water for sixty days and nights, by which treatment its percentage of Fe_2O_3 was

increased to 83.33 only; on further washing the wash-water still contained sulphuric acid, no limit to the decomposition appearing to exist.

It is possible that the basic sulphate, precipitated in the first instance by the dilution of a strong solution of the normal sulphate, may be pure $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ (80 per cent. Fe_2O_3), and that this is subsequently rendered richer in iron by the decomposing action of the water; the evidence, however, which we have on the subject is not sufficient to justify such a conclusion.

The sulphates obtained in the above experiments were orange-yellow flocculent precipitates, which on being dried assumed a darker colour, the depth of which depended on the temperature of their desiccation.

III. *Precipitation by an Alkaline Carbonate.*

When the ferric sulphate solution was diluted with ordinary instead of distilled water, not only was the basic sulphate precipitated at once, but the amount precipitated was more abundant, and in composition it did not differ appreciably from $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$; since common boiled water acted exactly like distilled water these differences must be due to the calcium carbonate present, and in order to investigate more thoroughly the action of a soluble carbonate on ferric sulphate a given amount of the solution of the latter salt was diluted with various quantities of a standard solution of sodium carbonate. The results thus obtained are embodied in Table II.

The addition of sodium carbonate in very small quantities to ferric sulphate causes only a darkening of the solution, and when as much as 0.15 mol. of the alkali has been added to each molecule of the sulphate present a small but appreciable amount of basic salt is precipitated after the lapse of some hours. With larger quantities of the carbonate the temporary formation of a precipitate of (probably) ferric carbonate is observed; this precipitate dissolves at once on agitation, evolving carbon dioxide and leaving a perfectly clear, dark-brown solution, which on standing gradually deposits the basic sulphate, carbon dioxide being evolved until the action is entirely finished. The time required for the completion of this action depends on the relative quantities of the reagents present. Thus, in Experiment 15, it was completed after the expiration of a few minutes, whereas for Experiment 8 over 24 hours were requisite. In a precisely similar manner the greater the relative quantity of alkaline carbonate present the sooner does the permanent precipitate of basic salt make its appearance.

TABLE II.—*Precipitation of $\text{Fe}_2(\text{SO}_4)_3$ by various Amounts of Na_2CO_3 .*Temperature 15°C .

Precipitates analysed 48 hours after the addition of the carbonate.

$\text{Fe}_2(\text{SO}_4)_3$.	Na_2CO_3 .	Water.	Fe_2O_3 contained in the precipitate, that in the $\text{Fe}_2(\text{SO}_4)_3$ taken being 100.	Percentage of Fe_2O_3 in the anhydrous precipitate.
4.† 5 c.c. = 1 mol.	0.62 mols.	100 c.c. = 1,900 mols.	7.6	79.77
5. " "	0.89 "	" "	31.5	79.36
6. " "	1.24 "	" "	50.0	79.29
7. " "	1.64 "	" "	66.6	79.16
8. " "	0.71 "	200 c.c. = 3,800 mols.	20.0	79.26
9. " "	1.07 "	" "	42.2	78.81
10. " "	1.60 "	" "	66.9	80.17
11. " "	2.13 "	" "	77.0	81.60*
12. " "	2.70 "	" "	87.0	88.38*
13. " "	2.84 "	" "	89.0	90.40*
14. " "	3.24 "	" "	98.0	98.85*
15. " "	4.27 "	" "	100.0	99.20*
16. " "	1.60 "	50 c.c. = 950 mols.	66.5	79.88
17. " "	1.60 "	100 " = 1,900 "	68.0	79.03
10. " "	1.60 "	200 " = 3,800 "	66.9	80.17
18. " "	1.60 "	500 " = 9,500 "	65.0	79.15

Table II shows that when the sodium carbonate is added in various amounts not exceeding 1.64 mol. for each molecule of ferric sulphate present, then the precipitate obtained is moderately constant in its composition, approaching very nearly to $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ (= 80 per cent. Fe_2O_3), but when the alkali exceeds this amount the precipitate becomes much richer in ferric oxide, its composition varying regularly according to the amount of sodium carbonate added, and consisting solely of this oxide when the quantity of alkali is about 3.3 mols. These precipitates moreover (Experiments 11—15) are distinctly different from those obtained by using a smaller amount of alkali, for instead of appearing orange and pulverulent on being dried at 100°C . they dry to a hard, black, friable mass, and this, when exposed to moist air, does not become hydrated without splitting up and spirting in every direction. These differences in appearance and behaviour are evidently due to the presence of uncombined ferric hydrate, a

† In this and several other of the experiments twice or thrice these quantities were taken.

very small admixture of this substance being sufficient to alter the appearance of the dried precipitate entirely, as is seen by comparing Experiments 10 and 11, all those cases in which the precipitates dried black being marked with an asterisk.

In every case where there is no uncombined ferric hydrate present I believe the precipitates to consist entirely of the pure basic sulphate, $2\text{Fe}_2\text{O}_3.\text{SO}_3$, the constant deficit in the percentage of ferric oxide found being due to their not having been washed thoroughly. All the experiments given in this table were performed before that one described on p. 809 had shown that these substances are but very slowly decomposed by being washed with cold water, consequently, in order to avoid any decomposition from this source, the precipitates were only washed so long as any iron salt continued to be detected in the wash-water; this washing, however, was apparently insufficient to remove all the sodium sulphate or uncombined sulphuric acid,* and hence the inaccuracy in the analytical numbers obtained. The first four experiments given in this table tend to confirm this view, for in their case the same volume of water was used to wash each of the precipitates, and this amount of water would wash the precipitate more thoroughly as the actual amount operated on was less; accordingly we see that the percentage of ferric oxide found is more nearly that required by theory in exact proportion as the amount of the precipitate obtained diminishes. The mean of the first four experiments (79.388 per cent. Fe_2O_3) is nearly identical with the mean of the other similar experiments which were less carefully performed (79.383), and the deficit of 0.62 per cent. of ferric oxide on the theoretical amount is not greater than what is rendered probable from Experiment 15, where the precipitate consists of ferric hydrate only.

Subsequently several of the above experiments were repeated, washing the precipitates three or four times longer than before, and in all of these cases the analytical numbers obtained were, within experimental error, those required by the formula $2\text{Fe}_2\text{O}_3.\text{SO}_3$.†

There can be little doubt therefore as to the existence of a definite basic sulphate, $2\text{Fe}_2\text{O}_3.\text{SO}_3$, or as to its being obtained either pure or mixed with uncombined ferric hydrate when the normal sulphate is decomposed by a smaller or larger amount of alkaline carbonate.

The numbers given in the fourth column show approximately the actual amount of the various precipitates obtained; when represented diagrammatically they form a tolerably regular curve which shows that

* Many basic salts and metallic hydrates retain an acid with far greater energy than a salt, and will sometimes even decompose a neutral salt, retaining its acids, and allowing the base to be washed away with facility.

† It is scarcely necessary to mention that the entire absence of any sodium or any carbonate in these precipitates was thoroughly proved.

the last portions of the ferric sulphate present require a considerably larger amount of the alkali to effect their decomposition than the first portions do; the curve also shows that the whole of the ferric sulphate is decomposed at nearly the same point at which the precipitate first consists of ferric hydrate only.

The last four experiments in the table show that an alteration in the amount of the water present has no appreciable effect on either the amount or the composition of the precipitate obtained.

Various experiments were made to determine how the point at which the uncombined ferric hydrate begins to be precipitated is influenced by an alteration in the temperature, and it was found that up to 42° C. very nearly the same results were obtained as at 15° C.; but at 65° C. 0.68 mol. of the carbonate precipitated some of the uncombined hydrate, and at 81 C. the limit of the precipitation of the pure basic salt was 0.58 mol.

IV. *Ferric Sulphate added to Various Quantities of Boiling Water.*

In these experiments 5 c.c. of the ferric sulphate solution were poured into various quantities of water, and the liquid, which became cloudy at once, was filtered as soon as the addition of the iron salt was complete. The results thus obtained are represented in curve No. 1, Plate I,* and show a regular rise in the percentage of Fe_2O_3 formed, from a little over that required by the formula $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, up to 84.42 per cent. No break in the curve or other indication of a more highly basic sulphate than $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ is seen. These precipitates are rather darker and less bulky than those previously described, but although containing more Fe_2O_3 than 80 per cent., they do not dry black and brittle, but orange and pulverulent,† showing that they contain no uncombined ferric hydrate similar to that contained by some of the former ones; it is possible, however, that ferric hydrate may be present in them, but in a different form to that present in the previous cases. As it was thought possible that in all these experiments the same sulphate (perhaps $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$) might have been precipitated at first, and subsequently altered to some other sulphate containing more Fe_2O_3 than 84.4 per cent. by a secondary action, which proceeds to a greater extent in cases where the quantity of water present is greater (perhaps through a greater amount of time being required for the filtration);

* Most of the single experiments plotted in this and other curves are the means of several.

† This is also the case with all the substances which were obtained in any of the other series of experiments hereafter described in which the application of heat was used.

other experiments were performed similar to the above, except that after the addition of the ferric sulphate the liquid was kept in a state of ebullition for one minute or for ten minutes, as the case might be, before it was filtered. The results are given in curves Nos. 2, 3, and 4; curve 4 it will be seen is the same in character, but different in position from 3, which difference is due to the two sets of experiments which these curves record having been performed in differently shaped flasks, and at different barometric pressures, and they show that strict attention to every circumstance which may influence the results is absolutely necessary to render these results at all comparable with each other.

At Experiment 33 there appears to be a sudden rise and alteration in the nature of the curve (No. 3); at this same point it was also observed that the basic sulphate precipitated was in a more finely divided condition, and consequently the filtration of the liquid required a much longer time than in the previous experiments, and had generally to be repeated. In order to ascertain whether this prolonged filtration could account for the irregularity in the curve, Experiment 33 was repeated, but, before being filtered, the liquid was allowed to cool to 35°C ., the result (Experiment 34 in the plate) showed that by this treatment the percentage of Fe_2O_3 was raised 0.75° above that in Experiment 33. Again, 5 c.c. of the ferric sulphate solution were boiled for ten minutes with 413 c.c. of water, and the liquid cooled to 56°C . before it was filtered, and in this case (Experiment 31) the percentage of Fe_2O_3 in the precipitate was 0.42 higher than at the corresponding point in the curve No. 3. These experiments tend to prove the correctness of the above explanation, and if in all the experiments the liquid could be filtered in the same time, the curve would probably continue in the direction of the dotted line. In curve 4 also, the similar irregularity which it exhibits about this point would disappear.

The wavy curves, Nos. 5, 6, and 7 represent series of experiments in which the time of ebullition, and not the quantity of water used, was the only variable factor.

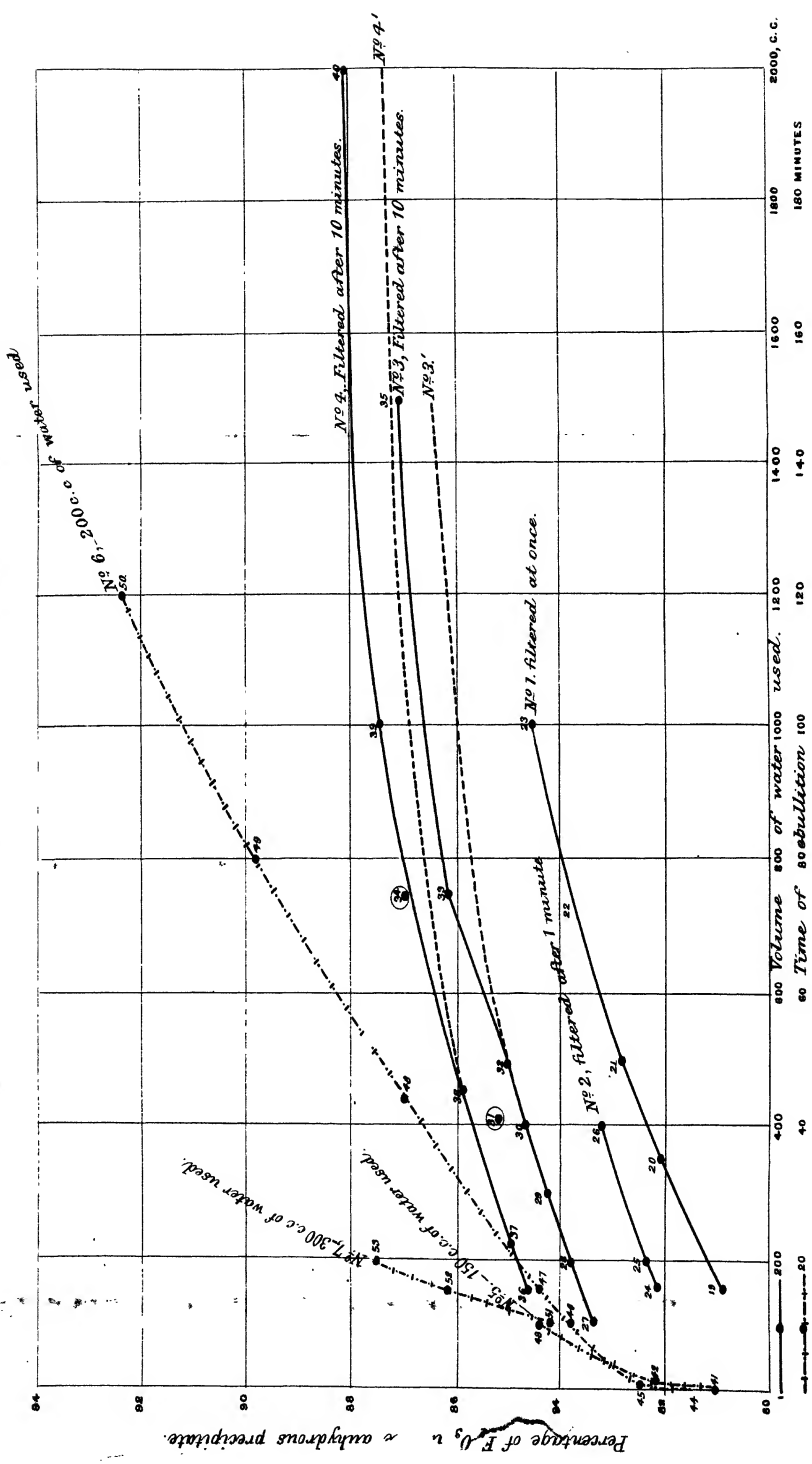
All the seven sets of experiments recorded in Plate I exhibit only a regular variation in results with the regular variation of any of the quantities influencing these results; in no case is there any trace of the existence of a definite basic sulphate containing a percentage of Fe_2O_3 , between the extreme limits 81 and 92.5.

V. *Weak Solutions of Ferric Sulphate heated below 100°C .*

In these experiments the ferric sulphate solution was diluted to the required strength, and then 200 c.c. of this weak solution were heated

PLATE I.

5 c.c. of $\text{Fe}_2(\text{SO}_4)_3$ solution added to various quantities of boiling water and filtered after various lengths of time.



in a 300 c.c. flask immersed in a water-bath; as soon as the first cloudiness was observed in the liquid, the lamp heating the bath was extinguished; the temperature of the liquid in the flask rose 5° or 6° C. higher, and was let cool through the same number of degrees before it was removed from the water-bath and filtered. The experiments were conducted so as to be as comparable as possible with each other. The heating and cooling occupied about 45 minutes. The results thus obtained are given in Table III.

TABLE III.—*Weak Solutions of Ferric Sulphate heated to Temperatures below 100° C.*

Percentage of $\text{Fe}_2(\text{SO}_4)_3$ contained in the solution.		Temperature at which the liquid becomes cloudy.	Percentage of Fe_2O_3 contained in the anhydrous precipitate.
54.	0.33	58° C.	80.01
55.	0.55	75	80.15
56.	1.10	87	81.44
57.	1.60	95	82.09
58.	2.08	99.5° C., then boiled	65.00

In Experiment 58 of this table the liquid, after becoming cloudy, was removed from the bath and boiled over the lamp for about 30 minutes, and the results show that when actual ebullition takes place, a totally different action occurs: the effect of boiling weak solutions of ferric sulphate will be fully discussed below. The other experiments given in the table exhibit great regularity, and when the numbers in both the second and third columns are represented diagrammatically, they give rise to remarkably uniform curves, showing no trace whatever indicative of a definite basic sulphate containing more than 80 per cent. of Fe_2O_3 .

On again heating some of the filtrates from the above precipitates, they became cloudy at a rather higher temperature, and the precipitates thus obtained were richer in Fe_2O_3 than those deposited in the first instances. Thus the filtrate from Experiment 54 deposited a precipitate containing 82.19 per cent. of Fe_2O_3 , and that from 56 deposited one containing 82.42 per cent.

VI. Repetition of Sheerer's Experiments.

Sheerer in 1838 (*Pogg. Ann.*, 44, 453) heated solutions of ferric sulphate of various strengths till they attained the boiling point, and then determined the amount and composition of the precipitates thus obtained; the strengths of the solutions used in his six experiments

were 1.0, 0.5, 0.25, 0.125, 0.1, and 0.01 per cent. respectively. The temperatures at which these liquids first became cloudy are not very concordant with those quoted in Table III; they would, however, be largely influenced by the manner in which heat was applied. The main point sought by Sheerer was to determine any relation which might exist between the amount of basic salts precipitated and the strength of the solution; the want of accordance in repeated experiments, however, prevented him succeeding in doing this. In the first three cases above cited the precipitates were analysed, and the percentage of ferric oxide contained by them was found to be 85.21, 85.6, and 85.32 respectively; accordingly he concluded that the sulphate precipitated in every case was a definite chemical compound, possessing the formula $3\text{Fe}_2\text{O}_3.\text{SO}_3$, which would contain 85.9 per cent. of Fe_2O_3 (or, according to the atomic weights used by Sheerer, 85.42). Unfortunately Sheerer does not state whether he separated the precipitate from the liquid as soon as the latter had reached 100°C ., or whether he allowed the ebullition to continue for some time, so that an exact repetition of his experiments is impossible. However, in order to get as much light as possible on the subject, one or two experiments (given in Table IV) were made, in which the solutions were heated over a rose burner and filtered as soon as they reached a state of thorough ebullition.

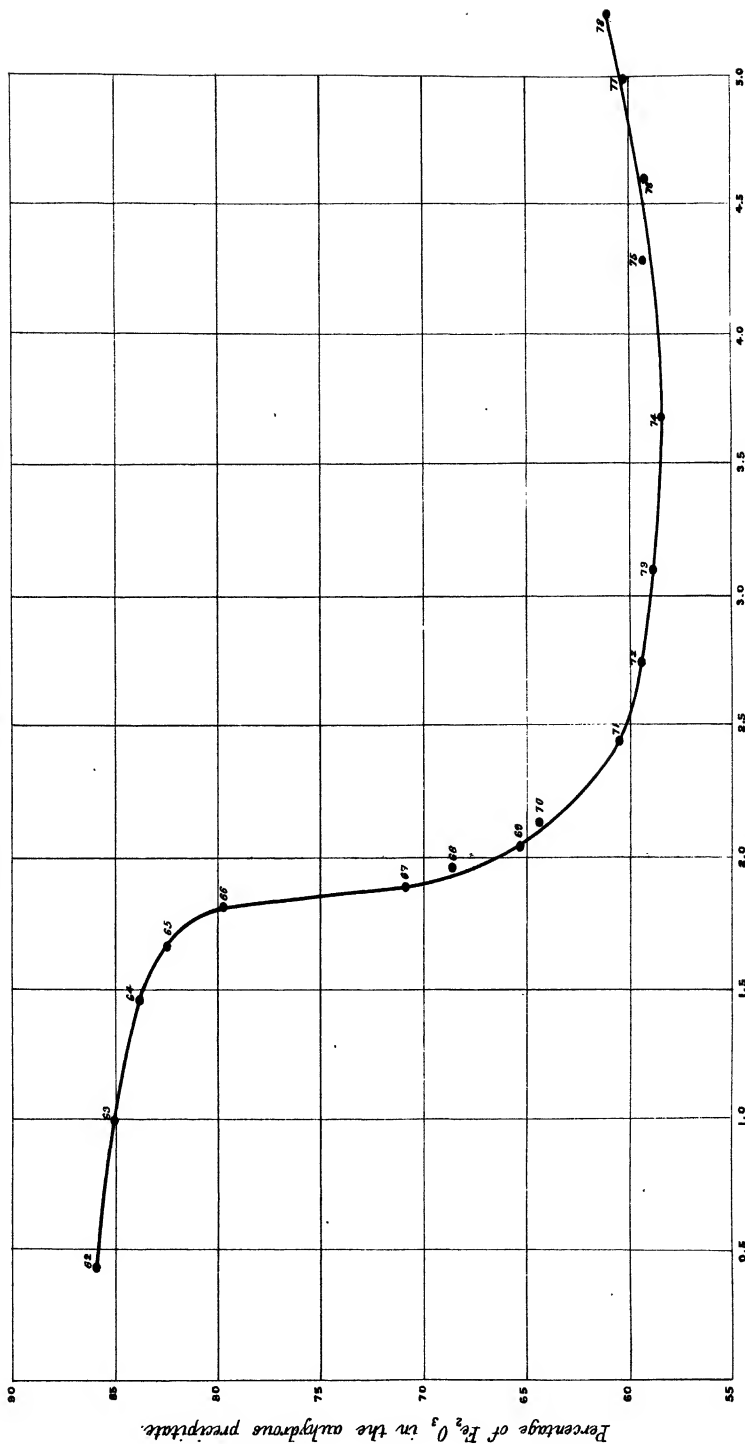
TABLE IV.—*Dilute Solutions of Ferric Sulphate heated to boiling and then filtered at once.*

* Percentage of $\text{Fe}_2(\text{SO}_4)_3$ in the solution.	Weight of anhydrous precipitate obtained per gram $\text{Fe}_2(\text{SO}_4)_3$.		Percentage of Fe_2O_3 in the anhydrous precipitate.	
	By Pickering.	By Sheerer.	Pickering.	Sheerer.
59. 1.0	0.0822 gram	0.1442 gram	81.33	85.21
60. 0.5	0.2224 "	0.257 "	81.99	85.6
61. 0.125	0.385 "	0.373 " ?	83.57	?

† Judging from the various quantities of the precipitates obtained, Sheerer probably boiled his solutions for several minutes before filtering them, and this would account for his precipitates being richer in iron than the others; but that his three analyses should have yielded very nearly the same numbers must be accidental, since the present experiments, in accordance with those discussed in the preceding paragraphs, show nothing but a regular variation in composition, and afford no evidence whatever of the existence either of $3\text{Fe}_2\text{O}_3.\text{SO}_3$ or of any other definite chemical compound.

PLATE II.

Solutions of ferric sulphate of various strengths boiled for 80 minutes.



Percentage strength of the ferric sulphate solution.

Percentage of Fe_2O_3 in the anhydrous precipitate.

VII. *Solutions of Ferric Sulphate boiled for 30 minutes.*

It has already been noticed in connection with Table III, that when a solution of ferric sulphate, which is too strong to become cloudy below $100^{\circ}\text{C}.$, is boiled, the precipitate thus obtained, instead of containing over 80 per cent. of Fe_2O_3 , is found to contain less than 70. In order to study more fully the alteration in the action which takes place at this point, the experiments which are represented in Plate II were performed.

In these experiments solutions of ferric sulphate of gradually increasing strengths were taken and boiled for a given length of time, 30 minutes. With the weaker solutions, which became cloudy before they had begun to boil, the precipitates were of a dark orange-red colour, and contained as much as 85 per cent. or more of ferric oxide. This percentage gradually diminished as the solutions taken became stronger, till, on reaching the point at which no cloudiness occurs before ebullition, the diminution became very sudden, the percentage of Fe_2O_3 soon falling as low as 65, and then more gradually reaching a minimum of 57, at which point it began to rise again, reaching 61 in the last experiment of the series.

At the same time as these basic sulphates became poorer in iron, they became gradually lighter in colour, being lemon-yellow when containing about 60 per cent. of Fe_2O_3 , or any amount under this. They were also less bulky, harder, and more pulverulent than the richer precipitates, being more easily washed and less rapidly decomposed by water; they were deposited more on the bottom and sides of the flask than in the liquid itself, and some portions which had become rather superheated, and probably dehydrated, were considerably darker than the rest. The formation of this crust is, as may easily be imagined, the cause of much bumping, and, in consequence, of the failure of many experiments; it was especially felt in the Experiments 64—66, where great difficulty was experienced in boiling the solution for so long as 30 minutes; it also was to a great extent the reason why many discordant results were obtained, and indeed it was only by taking the mean of a large number of experiments at each point that a curve of tolerable uniformity could be drawn, especially at the more sudden part of it between Experiments 64 and 71.

The first experiments performed gave rise to the expectation that this curve would lead to the recognition of a sulphate containing 60 per cent. of Fe_2O_3 , which would correspond to the formula $3\text{Fe}_2\text{O}_3.4\text{SO}_3$; this expectation, as it is seen, proved vain, the percentage of Fe_2O_3 falling without break or irregularity to a considerable distance below 60 (as it also does in other series of experiments to be described below); and it must be remarked, the causes of inaccuracy in the analyses of the pre-

precipitates obtained by sodium carbonate (difficulty of washing, and decomposition by water) are here reduced to a minimum and are quite inappreciable. The rise in the last part of the curve is curious, but should be less marked than it is here, it being partially, but not entirely, due to an accidental circumstance which was not recognised till some subsequent experiments were performed (§ XII), in connection with which it will be described and discussed.

The only conclusion, therefore, to be drawn from this curve is, that it affords no evidence whatever as to the existence of any definite basic sulphate.

VIII. *Solutions of Ferric Sulphate boiled for various Lengths of Time.*

In order to ascertain the effect of altering the time of ebullition, the experiments given in Table V were performed; the sets at the top and at the bottom of this table show that when the precipitates contain over 83 or under 60 per cent. of Fe_2O_3 , their composition is, within the limit of experimental error, unaffected by a considerable alteration in the time; but when the experiments are made at points which occur in the more abrupt part of the curve in Plate II (*i.e.*, if the precipitates contain between 80 and 60 per cent. Fe_2O_3), then the time of the ebullition becomes an important factor in the composition of the precipitate, this latter becoming poorer in ferric oxide as the time allowed is longer.

TABLE V.—*Solutions of Ferric Sulphate boiled for various Lengths of Time.*

Percentage of $\text{Fe}_2(\text{SO}_4)_3$ in the solution taken.		Relative weights of the precipitates obtained.	Time of ebullition.	Percentage of Fe_2O_3 in the anhydrous precipitate.
79.	1·46	—	14 minutes	83·71
80.	1·46	—	17 "	83·81
81.	1·46	—	30 "	83·60
82.	1·8	—	15 "	81·35
83.	1·8	—	45 "	74·47
84.	2·1	0·0761 gram.	5 "	76·19
85.	2·1	0·1874 "	10 "	74·40
86.	2·1	0·397 "	15 "	72·55
87.	2·1	1·511 "	30 "	64·33
88.	3·08	—	30 "	58·94
89.	3·08	—	45 "	58·81

IX. Solutions of Ferric Sulphate heated to 100° C. without Actual Boiling.

In Table VI are given the results of experiments in which the solutions of ferric sulphate were heated at 100° C. for various lengths of time in a manner which prevented loss of water by evaporation, side by side with parallel experiments in which this loss was allowed to take place.

In Experiments 90, 91, and 93, the liquid was heated in a partially corked flask, so as to be at a temperature just below the boiling point, small bubbles of steam being given off now and then. In Experiment 92 the liquid was kept in full ebullition, but the flask was fitted with an inverted Liebig's condenser; in the two remaining experiments the solution was boiled in an open flask.

TABLE VI.—*Solutions of Ferric Sulphate boiled in Various Ways.*

Percentage strength of the solution.	Manner of ebullition.	Time allowed.	Relative amounts of precipitate obtained.	Percentage of Fe_2O_3 in the anhydrous precipitate.
90. 2·1	In partially closed flask	30 minutes	0·761	77·02
87. 2·1	In an open flask	30 „	1·511	64·33
91. 2·1	In partially closed flask	15 „	0·217	74·95
92. 2·1	In flask with Liebig's condenser	15 „	0·528	78·05
86. 2·1	In an open flask	15 „	0·397	72·55
93. 3·01	In partially closed flask	15 „	0·188	58·93
94. 3·01	In an open flask	15 „	0·198	58·80

These experiments only show that when evaporation takes place, the precipitate is less rich in Fe_2O_3 than when no evaporation takes place, and that this difference becomes inappreciable when the precipitates contain less than 60 per cent. Fe_2O_3 . From the relative amounts of basic sulphate obtained in the various cases, no conclusions can be drawn.

X. Attempts to Ascertain whether the Precipitate is Altered during the Ebullition.

The question which naturally arises from a study of the above experiments is, whether the precipitate which is thrown down during the first stages of the ebullition remains unaltered in composition when once precipitated, or whether it is altered continuously by a continuation of the boiling.

In order to obtain some light on this point, solutions were boiled for various times, and filtered twice or thrice during the ebullition, in which way the precipitates deposited from the liquid during various stages were collected separately and analysed. The results thus obtained with a 2·1 per cent. solution are given below in Tables VII—IX:—

TABLE VII.—*Solutions Boiled for 10 Minutes.*

85. Boiled for 10 mins. consecutively.

Precipitate obtained = 0·1874 gram (or 0·0927 gram per 5 mins.), and contains 74·40 per cent. Fe_2O_3 .

Boiled for 10 mins. in two intervals of 5 mins. each.

95. Precipitate obtained during first 5 mins. = 0·0761 gram, and contains 76·19 per cent. Fe_2O_3 .

96. Precipitate obtained during second 5 mins. = 0·0631 gram, and contains 75·18 per cent. Fe_2O_3 .

Hence, precipitate obtained during 10 mins. when divided into two intervals of 5 mins. each, = 0·14 gram (or 0·07 gram per 5 mins.), and contains 75·73 per cent. Fe_2O_3 .

TABLE VIII.—*Solutions Boiled for 15 Minutes.*

86. Boiled for 15 mins. consecutively.

Precipitate obtained = 0·397 gram (or 0·132 gram per 5 mins.), and contains 72·55 per cent. Fe_2O_3 .

Boiled for 15 mins. in three intervals of 5 mins. each.

95. Precipitate obtained during first 5 mins. = 0·0761 gram, and contains 76·19 per cent. Fe_2O_3 .

96. Precipitate obtained during second 5 mins. = 0·0631 gram, and contains 75·18 per cent. Fe_2O_3 .

97. Precipitate obtained during third 5 mins. = 0·0283 gram, and contains 67·95 per cent. Fe_2O_3 .

Hence, precipitate obtained during 15 mins., when divided into three intervals of 5 mins. each, = 0·1675 gram (or 0·0558 gram per 5 mins.), and contains 74·42 per cent. Fe_2O_3 .

TABLE IX.—*Solutions Boiled for 30 Minutes.*

87. Boiled for 30 mins. consecutively.

Precipitate obtained = 1·511 gram (or 0·252 gram per 5 mins.), and contains 64·33 per cent. Fe_2O_3 .

Boiled for 30 mins. in two intervals of 15 mins. each.

86. Precipitate obtained during first 15 mins. = 0.397 gram (or 0.132 gram per 5 mins.), and contains 72.55 per cent. Fe_2O_3 .
 98. Precipitate obtained during second 15 mins. not sufficient to analyse.

Hence, precipitate during 30 mins., when divided into two intervals of 15 mins. each, = rather more than 0.397 gram (or 0.132 gram per 5 mins.), and contains (probably) rather less than 72.55 per cent. Fe_2O_3 .

Boiled for 30 mins. in four intervals of 5, 5, 5, and 15 mins. respectively.

95. Precipitate obtained during first 5 mins. = 0.0761 gram, and contains 76.19 per cent. Fe_2O_3 .
 96. Precipitate obtained during second 5 mins. = 0.0631 gram, and contains 75.18 per cent. Fe_2O_3 .
 97. Precipitate obtained during third 5 mins. = 0.0283 gram, and contains 67.95 per cent. Fe_2O_3 .
 99. Precipitate obtained during last 15 mins. = 0.0937 gram, and contains 65.16 per cent. Fe_2O_3 .

Hence, precipitate obtained during 30 mins., when divided into four intervals of 5, 5, 5, and 15 mins. respectively, = 0.261 gram (or 0.0435 gram per 5 mins.), and contains 71.097 per cent. Fe_2O_3 .

On comparing the first and last data in each of these tables, it at once becomes apparent that the experiments recorded here can throw no light on the point in question, for when the time of ebullition is divided into two or more intervals, the amount of precipitate obtained is far less than when the boiling is uninterrupted, in addition to which the basic sulphate in the former case invariably contains considerably more ferric oxide than in the latter case, showing that the experiments under these different circumstances are in no way comparable with each other. They, however, bring to light a somewhat interesting circumstance in the reaction, namely, that the particular state of dissociation of the normal sulphate which it is necessary to induce before the formation of the basic sulphate takes place, is not attained at once, but requires time for its production; thus, taking the experiments in Table VII, which present the least complicated case, we find that 0.0761 gram is precipitated in the first 5 mins., and hence, in the case where the ebullition is continued without interruption (Experiment 85), 0.1113 gram in the second 5 mins.; whereas when the interval requisite for the filtration and reheating of the solution (about 8 mins.)

allowed between the first and second 5 mins., then the conditions favourable for the formation of the basic sulphate are so far disturbed that during the second of these intervals only 0·0631 gram instead of 0·1113 gram is formed; and at the same time that which is deposited is much less rich in ferric oxide than in the other case. In Table IX a still more striking example of this is seen, where, in Experiment 98, instead of 1·114 gram being deposited, the amount obtained was not nearly sufficient for analysis.

A regular decrease in richness in Fe_2O_3 of the precipitates obtained during successive periods in the ebullition, will also be noticed.

These experiments, therefore, give no grounds whatever for assuming that the precipitates obtained are mixtures of two or more definite basic sulphates.

XI. *Repeated Boiling of the same Solution.*

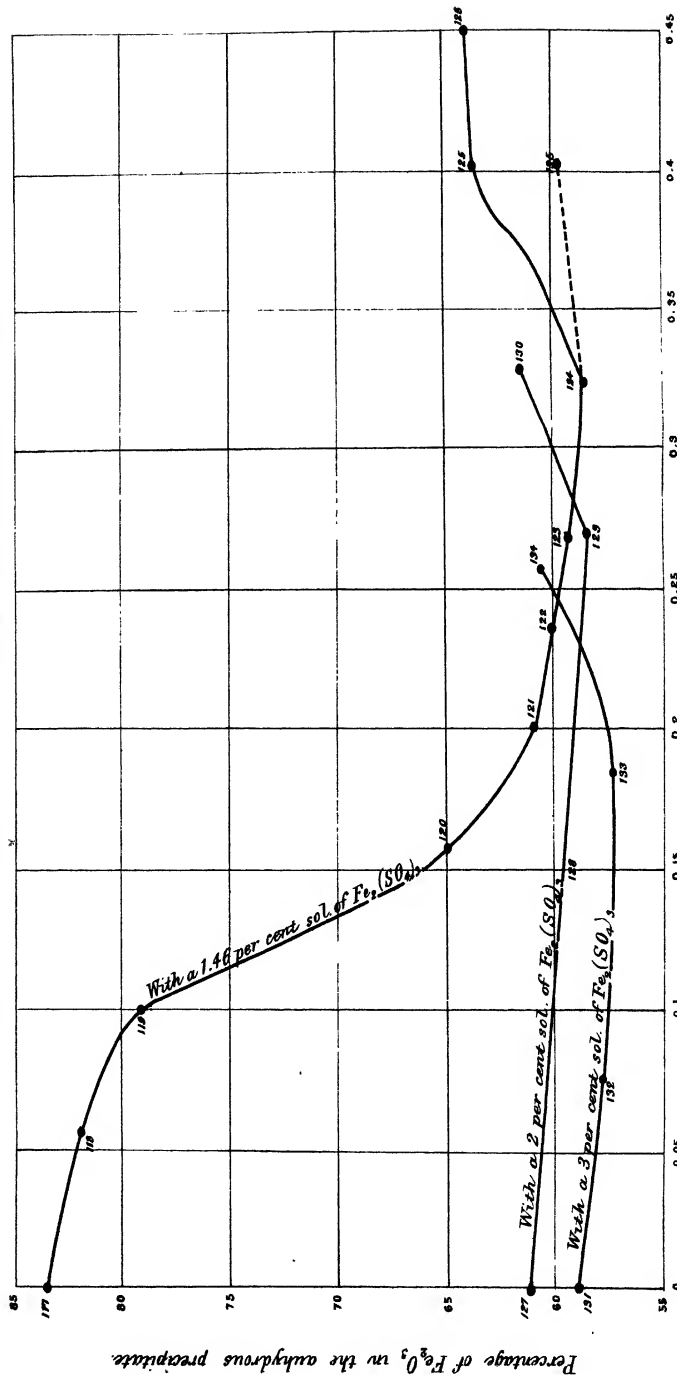
The filtrates from some of the above experiments were made up to their original volumes and boiled again for the same lengths of time as in the original cases; this operation was repeated several times, and the results obtained from the analysis of the various precipitates produced are given in Table X.

TABLE X.—*Repeated Boiling of the same Solution.*

Percentage of $\text{Fe}_2(\text{SO}_4)_3$ in the original solution.	No. of the boiling.	Time of ebullition.	Amount of precipitate obtained.	Percentage of Fe_2O_3 in the anhydrous precipitate.
100 2·08	First	60 minutes	1·047 gram	61·45
101 "	Second	"	0·4287 "	60·67
102 "	Fourth	"	0·2400 "	60·33
103 "	Fifth	"	0·2430 "	58·48
104 "	Sixth	"	0·1944 "	57·38
105—108 "	Seventh to tenth	"	{ Amount of precipitate about 0·2 gram in each case }	—
109 2·13	First	45 minutes	1·570 gram	64·07
110 "	Second	"	0·1803 "	63·56
111 "	Third	"	0·1060 "	62·90
112 "	Fourth	"	{ 0·3050 " =	—
113 "	Fifth	"	{ 0·1525 " each	62·62
114 3·45	First	30 minutes	0·4001 gram	58·86
115 & 116 "	Second and third	" each	0·1353 " =	59·28
			0·0676 " each	

PLATE III.

Solutions of ferric sulphate boiled for 30 minutes with varying quantities of sulphuric acid.



These experiments show that a very rapid decrease in the amount of the precipitate obtained takes place at first, but that it soon becomes smaller till the amount precipitated becomes very nearly constant. The percentage of Fe_2O_3 found by analysis exhibits a steady and continuous decrease, the slight rise observed in the last experiment being probably due to an accidental circumstance, which will be explained in the next paragraph.

XII. *Solutions of Ferric Sulphate Boiled with various Amounts of Sulphuric Acid.*

In the following experiments the solutions of ferric sulphate were mixed with various quantities of free sulphuric acid and then boiled for 30 minutes: the results thus obtained are represented in the curves given in Plate III.

The curve representing experiments with a 1.46 per cent. solution bears the same general character as that in Plate II, while the other two curves are similar to the last portions of it.

In all the experiments in which a solution of ferric sulphate is boiled, a small brown deposit is formed on the superheated portions of the flask above the level of the liquid; this deposit was unfortunately always included in the analysis of the main precipitate, and where the amount of this latter is large it can have little or no appreciable effect on the analytical numbers obtained; but, in the experiments which form the last part of the curves, the main precipitate becomes very small in amount, and this deposit would introduce a sensible error in the analysis unless it had the same composition as the precipitate itself. In order to ascertain whether this was the case or not, Experiment 125 was repeated, the brown deposit being removed from the precipitate at the bottom of the flask and not analysed with it; the analytical numbers obtained (Experiment 135) show that this brown deposit must contain more ferric oxide than the main precipitate, and that the rise at the end of the curve is principally, but not entirely, due to this fact; similarly with the other curves in the same plate, and also with that in Plate II.

In order to see whether any of the sulphuric acid present was carried away with the steam during the ebullition, some water was mixed with as much acid as the maximum used in the above experiments and boiled for 30 minutes, the steam being conducted by a very wide tube into a flask containing litmus water; at the end of the time allowed sufficient acid had been carried over to colour the litmus red, but its amount was so small that it was practically quite inappreciable. Hence, reverting to the experiments in Tables VII, VIII, and IX, we find that there are two causes which tend to make the precipitate

deposited during the later periods of the ebullition less rich in Fe_2O_3 , than that deposited during the earlier parts, the one being the concentration of the solution, the other, the increase in the relative proportion of acid to metallic oxide present, since by the precipitation of the basic substance a comparatively larger portion of Fe_2O_3 than of SO_3 is thrown down; at the same time the tendency which both these causes have to diminish the actual amount of the basic sulphate obtained is more than counterbalanced (in the cases where the ebullition is uninterrupted) by the state of greater dissociation induced by prolonged heating.

The conclusions, therefore, which may be drawn from the experiments in Plate III are, like those drawn from Plate II, of an entirely negative character, not indicating the existence of any definite chemical compound.

XIII. *Partial Solution of the Precipitates in Hydrochloric Acid.*

In dissolving the above precipitates in hydrochloric acid it was noticed that when containing less than 80 per cent. of ferric oxide they appeared to dissolve in two or more stages, as if they consisted of two or three different but definite substances, which differed in the ease with which they were dissolved by the acid, the darker being the most readily soluble. In order to ascertain whether this was so or not, the experiments given in Table XI were performed.

Although two of these experiments (140 and 141) give numbers which represent within the limits of possible error the basic sulphate, $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$ (containing 60 per cent. Fe_2O_3), the others show that this accordance must be accidental, and that where the precipitates are treated with hydrochloric acid they dissolve gradually, the portions richer in iron dissolving before those which are poorer in iron, without any break in the continuity or other indication of the presence of any definite chemical compound.

TABLE XI.—*Partial Solution of the Precipitates in Hydrochloric Acid.*

136. Precipitate obtained by boiling a 2.23 per cent. solution of $\text{Fe}_2(\text{SO}_4)_3$ for 30 mins., and containing 63 per cent. Fe_2O_3 , treated with cold strong HCl till of a light yellow colour, and apparently homogeneous, then analysed, and found to contain 58.56 per cent. Fe_2O_3 .

137. The above experiment repeated with a precipitate obtained by boiling a 1.8 per cent. solution of $\text{Fe}_2(\text{SO}_4)_3$. The precipi-

tate contained 79.6 per cent. Fe_2O_3 , and the part difficultly soluble in HCl was found to contain 59.453 per cent. Fe_2O_3 .

-
- A precipitate containing 64.4 per cent. Fe_2O_3 treated with warm and weak HCl till light yellow and homogeneous; then, after being washed, was treated with stronger acid, till of a very light yellow, when the solution thus obtained was
138. found to contain 0.246 gram of a basic sulphate with 58.83 per cent. Fe_2O_3 , while the remaining undissolved portion (0.08 gram) contained 57.40 per cent. Fe_2O_3 .
-

- A precipitate containing 62 per cent. Fe_2O_3 digested with warm weak HCl till light yellow and homogeneous, and then treated thrice with successively stronger solutions of acid till entirely dissolved.
140. By the first treatment 1.444 gram of a sulphate containing 60.04 per cent. of Fe_2O_3 was dissolved.
141. By the second treatment 0.2355 gram of a sulphate containing 60.12 per cent. of Fe_2O_3 was dissolved.
142. The remainder consists of 0.0907 gram of a sulphate containing 59.23 per cent. of Fe_2O_3 .
-

- 10 grams of a precipitate containing 58.31 per cent. of Fe_2O_3 were dissolved in HCl in four portions as in the above experiments.
143. By the first treatment, 0.3702 gram of a sulphate containing 58.73 per cent. of Fe_2O_3 was dissolved.
143. By the second treatment, 0.3343 gram of a sulphate containing 58.35 per cent. of Fe_2O_3 was dissolved.
144. By the third treatment, 0.2255 gram of a sulphate containing 58.55 per cent. of Fe_2O_3 was dissolved.
145. The remainder consisted of 0.0700 gram of sulphate containing 56.42 per cent. of Fe_2O_3 .
-

XIV. *Reaction between Metallic Iron and Ferric Sulphate.*

Berzelius (*Gilb. Ann.*, **40**, 293) describes an experiment in which he digested a piece of metallic iron with a solution of ferric sulphate for some time at 30—40° C., a precipitate of a basic sulphate containing 60.73 per cent. of Fe_2O_3 being obtained, from which he concludes that the sulphate, $3\text{Fe}_2\text{O}_3 \cdot 4\text{SO}_3$ (= 60 per cent. Fe_2O_3), is formed in this reaction.

In order to repeat these experiments, pieces of iron wire, weighing about 5 grams, were digested with solutions of ferric sulphate of

various strengths and at various temperatures; the results of these experiments are given in Table XII.

TABLE XII.—*Action of Iron on Ferric Sulphate.*
Five grams of Iron digested with 3·5 grams of $\text{Fe}_2(\text{SO}_4)_3$.

Percentage strength of the $\text{Fe}_2(\text{SO}_4)_3$ solution.		Temperature.	Approximate amount of precipitate obtained.	Percentage of Fe_2O_3 in the anhydrous precipitate.	Remarks.
146	11·0	20° C.	0·0960	82·16	Action complete. The precipitate contained uncombined ferric hydrate.
147	3·5	20	0·1545	81·89	Action complete.
148	0·86	20	0·4706	81·06	"
147	3·5	20° C.	0·1545	81·89	Action complete.
149	3·5	35—45	0·2731	81·35	"
150	3·5	20° C.	0·053	77·80	Action about one-third complete.
151	3·5	20	0·1016	78·71	Action about two-thirds complete.
147	3·5	20	0·1545	81·89	Action complete.

From these experiments it will be seen that the composition of the precipitate invariably approximates that required by the formula $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$ (80 per cent. Fe_2O_3), there being in the extreme cases an excess or deficit of 2 per cent. of Fe_2O_3 . The amount of the precipitate increases, and its richness in iron diminishes, as the solution operated on is more dilute; and in the case where the solution contained as much as 11 per cent. of the sulphate, the precipitate obtained had a gelatinous appearance, and dried black and hard, showing it to contain uncombined ferric hydrate. The time required for the total reduction of the ferric sulphate was found to vary considerably, being increased by a diminution in the strength of the solution, and diminished by an increase in temperature. Thus, for instance, in Experiment 146 with an 11 per cent. solution, the action was complete in less than 12 hours; with a 3·5 per cent. solution in about 26 hours; and in Experiment 148 with an 0·86 per cent. solution it was just complete in 74 hours; while in the experiment at a higher temperature (No. 149) about 5 hours only were requisite. Throughout the action bubbles of hydrogen continued to be evolved.

From the action on the metallic iron being unequal in different parts, a considerable number of particles of that metal became detached, and

rendered it extremely difficult to determine the amount of the precipitate obtained, or the quantity of iron dissolved, with any attempt at accuracy; while, at the same time, they endangered the correctness of the analytical numbers obtained. In some of the experiments, no doubt, the percentage of Fe_2O_3 found in the precipitates was raised from this cause; but in others where the metallic particles were entirely eliminated, they were still found to contain considerably (1—1·5 per cent.) more Fe_2O_3 than 80 per cent., so that the sulphate $2\text{Fe}_2\text{O}_3\cdot\text{SO}_3$ does not appear to be the final product of the reaction.

An increase in temperature increases the amount, and slightly diminishes the richness in Fe_2O_3 of the precipitate.

During the first part of the action the basic sulphate contains considerably less than 80 per cent. Fe_2O_3 .

These experiments, therefore, afford no confirmation whatever of Berzelius's work, nor do they give any evidence as to the existence of the sulphate $3\text{Fe}_2\text{O}_3\cdot 4\text{SO}_3$, or of any other definite chemical compound.

XV. Conclusion.

The following is a list of the ferric sulphates which are stated to exist according to various authorities on the subject:—

- | | |
|---|--|
| 1. $\text{Fe}_2\text{O}_3\cdot 7\text{SO}_3$. | 9. $\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 2. $2\text{Fe}_2\text{O}_3\cdot 7\text{SO}_3$. | 10. $4\text{Fe}_2\text{O}_3\cdot 3\text{SO}_3$. |
| 3. $2\text{Fe}_2\text{O}_3\cdot 5\text{SO}_3$. | 11. $2\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 4. $3\text{Fe}_2\text{O}_3\cdot 7\text{SO}_3$. | 12. $3\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 5. $\text{Fe}_2\text{O}_3\cdot 2\text{SO}_3$. | 13. $4\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 6. $3\text{Fe}_2\text{O}_3\cdot 5\text{SO}_3$. | 14. $6\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 7. $2\text{Fe}_2\text{O}_3\cdot 3\text{SO}_3$. | 15. $7\text{Fe}_2\text{O}_3\cdot\text{SO}_3$. |
| 8. $3\text{Fe}_2\text{O}_3\cdot 4\text{SO}_3$. | |

The percentage of ferric oxide contained in these bodies varies between 22·22 and 93·33.

The references to their literature are as follows:—Berzelius, *Gölb. Ann.*, N.F., **7**, 304, 1811; Berzelius, *Gölb. Ann.*, **40**, 293, 1812; Mans, *Pogg. Ann.*, **11**, 75, 1827; Soubeiran, *Pogg. Ann.*, **20**, 173, 1830; Rose, *Pogg. Ann.*, **28**, 309, 1833; Sheerer, *Pogg. Ann.*, **40**, 104, 1837; Sheerer, *Pogg. Ann.*, **44**, 453, 1838; and **45**, 188, 1838; Anthon, *Repert. für d. Pharm.*, **81**, 237, 1843; Wittstein, *Buchner's Repert.*, 3te R., Bd. I, 185, 1848; Field, *Chem. Soc. J.*, 1862, 156; Muck, *J. pr. Chem.*, 1866, 103; Frenzel, *Jahrb. für Mineralogie*, 1875, 673; Meister, *Ber.*, **8**, 771, 1875; Monsel, see Würtz's *Dict. de Chemie*, T. I, section 2me, 1422.

A study of these papers leads to very unsatisfactory conclusions, and tends to throw discredit on the identity of all the fifteen sul-

phates; the body $\text{Fe}_2\text{O}_3 \cdot 2\text{SO}_3$ is perhaps the one which is best authenticated, and, even in this instance, we find that the strongest piece of evidence which can be adduced in favour of its existence is based on a single analysis of a solitary specimen of a mineral.

The experiments detailed in this paper prove the definiteness of the sulphate $2\text{Fe}_2\text{O}_3 \cdot \text{SO}_3$, and tend to disprove the existence of any other; they also show that by altering certain factors in the reaction, sulphates containing any required percentage of ferric oxide between 92 and 56 may be obtained, and, if these basic bodies are to be considered as ordinary and definite chemical compounds, we must conclude that they are mixtures of ferric oxide (or a very highly basic sulphate) and a sulphate containing less than 56 per cent. of Fe_2O_3 , in various proportions. This latter sulphate has, however, never been obtained, nor have we any evidence whatever as to its existence, unless, indeed, these experiments may themselves be considered as such.

LXXV.—*On the Colour-properties and Relations of the Metals, Copper, Nickel, Cobalt, Iron, Manganese, and Chromium.*

By THOMAS BAYLEY.

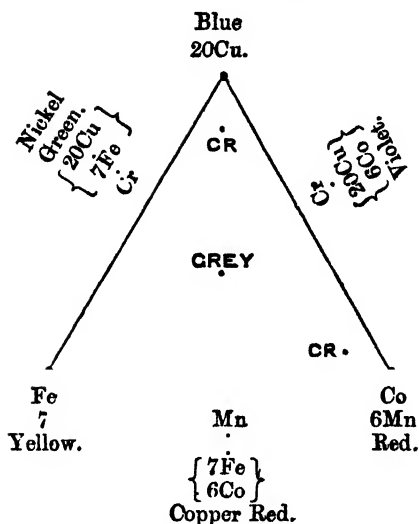
THE metals chromium, manganese, iron, cobalt, nickel, and copper form a group of elements with atomic weights progressing from 52.2 to 63.00, the mean lying somewhere between 57 and 58. They are characterised by salts corresponding to their normal oxides, which in dilute solution possess strongly developed and characteristic colours. The two lower members of the group belong to the even series in Mendelejeff's classification, the highest member, copper, to the odd elements, and the three intermediate members, iron, cobalt, and nickel, are part of the eighth series which links the odd and even elements together.

The partial investigation of the colour-properties of some of the elements of this group having revealed certain definite relations between them, it appeared probable that a comparative examination of the whole series might bring to light interesting and valuable information, and some experiments with iron, copper, and cobalt were instituted. Standard solutions were prepared containing 5 grams of each metal per litre; the copper and iron were weighed as metal, and the cobalt as sulphate after ignition to low redness. The iron was dissolved in dilute sulphuric acid, and oxidised with nitric acid, and the other solutions contained excess of both these acids. It became apparent on the first observation, that, on mixing the three solutions, a partial or total loss of colour resulted, and that at the same time the

liquid acquired the property of opacity, that is, of suppressing a certain portion of the white light passing through it.* On further trial it was found easy to mix the solutions so as to produce a neutral grey liquid. The proportions in which the metals must co-exist to give this optical neutrality were determined by trial in the following manner. A number of dry cylinders of white glass having been prepared, measured quantities of the standard solutions were placed in them in the proportions which seemed to give the nearest approach to an optically neutral liquid. The mixtures were then poured into tubes 20 centimeters long, closed at the ends by plates of glass. By looking through the columns and comparing the appearance with that presented by two partially crossed Nicol's prisms, situated at each end of a similar 20-centimeter tube, and by repeatedly making trial solutions, according as the result of the comparisons indicated, I found that perfect greyness is obtained by mixing 20 parts of the copper solution, 7 of the iron, and 6 of the cobalt. The solution so constituted appears in the 20-centimeter tube to be quite devoid of colour, but it suppresses a portion of the white light, and so causes the sky, or a white object viewed through it, to lose a portion of its brightness.

Cobalt, iron, and copper thus form a natural colour group, and their "colour-equivalents" are 20, 7, and 6 respectively, but these numbers must be considered to be tolerably close approximations only. The "colour-equivalents" are the numbers expressing the quantities of the metals required to produce an optically neutral mixture; the "colour-coefficients" are the reciprocals of the colour-equivalents, reduced to terms of the coefficient of copper as unity, and the colour coefficient of each element expresses the specific chromatic power of the element in the particular combination. For the present these terms must be taken to mean neither more nor less than this; but we shall find afterwards that it is possible to extend the definitions. The term "colour-coefficient" has already been used in this sense on discussing the colour relations of nickel and cobalt (*Proc Roy. I. A.*, 3, Ser. 2nd, Science); the colour-coefficient of iron, and possibly the coefficients of the other metals to a less extent, vary with the temperature; the determinations described above were made at about 18° C. The variation is insignificant for a few degrees, but if the neutral solution prepared at 18° be heated to boiling, the equilibrium is palpably disturbed, and the yellow colour of iron predominates. The colour-coefficient of iron also varies with the nature of the acid radical; the coefficient of iron dissolved in nitric acid is less than the coefficient of iron dissolved in sulphuric acid and oxidised with nitric acid.

* A brown mixture of iron, cobalt, and copper sulphate has been used by Vernon Harcourt as a standard in gas testing.



The relations of the solutions of the metals of this group are indicated in the accompanying diagram, where Cu, Fe, and Co are placed at the vertices of a triangle; any one of them is complementary to a definite mixture of the other two; iron is complementary to a mixture of cobalt and copper (violet), and cobalt to a mixture of iron and copper (green). A solution of a nickel salt is green, and by mixing iron and copper we can simulate the appearance of the nickel solution so closely, that the eye can detect no shade of difference. It is worthy of notice that the mean of the atomic weights of iron and copper, 59·5, is very near to the atomic weight of nickel. The mixture of iron and copper that most closely resembles nickel is not that which is complementary to cobalt. Such a solution contains an excess of iron, and therefore when mixed with cobalt, yields an opaque liquid, to which a decided yellow tinge is added. This is also what a mixture of cobalt and nickel in equivalent colour-proportions yields: therefore the analogy between the relations of the atomic weights of these elements and their chromatic relations is very close, for the atomic weight of nickel is sensibly lower than the mean of the atomic weights of iron and copper (59·5), that is, it approaches more nearly to the former than to the latter.

A copper solution is complementary to a mixture of iron and cobalt, and a copper solution is complementary to the reflection from the surface of copper; it follows then that the light transmitted by a mixture of iron and cobalt is similar to that reflected from copper. The truth of this assertion is apparent, as a dilute solution containing 7 parts of iron and 6 parts of cobalt has the peculiar red appearance characteristic of polished copper.

The chromatic properties of a metallic solution seem to be the result of several circumstances. The mean wave-length of the light absorbed by iron, nickel, cobalt, and copper increases as the atomic weight increases; the mean wave-lengths of the light absorbed by nickel and cobalt are nearly identical, because the light transmitted by cobalt contains the red and yellow, and the violet rays of the spectrum, and the light from nickel contains the rays composing the remainder of the spectrum, together with an excess of yellow rays common to both.

Speaking generally, we may say that the affinity of the metals of this group for oxygen increases with the colour-coefficients.

The colour-coefficients are in this order:—

Cu.	(Ni).	Fe.	Co.	Cr.Mn or Mn.Cr P
1	(1.05 about).	2.85	3.33	—

and this is the order which expresses the facility with which the oxides can be reduced by hydrogen, speaking roughly; it also expresses the electro-chemical order in which the metals follow each other when immersed in dilute nitric and sulphuric acids. This is Faraday's classification—copper, nickel, iron.

In speaking of the colour-properties of these metals I have in all instances referred to the salts corresponding to those oxides I have elsewhere (*Phil. Mag.*, Feb., 1879) distinguished as the normal oxides, in contradistinction to the protoxides on the one hand and the peroxides on the other. The solutions of the salts corresponding to the protoxides are usually either colourless or have an extremely faint colour.

Copper and chromium have colourless proto-salts, and the proto-salts of iron and manganese appear slightly coloured in concentrated solution. The proto-salts of manganese are sometimes said to be colourless, but I have always found them, when pure, to possess a faint rose tint resembling that of cobalt.* That this tint is not due to cobalt is evident from the fact that ammonium sulphide throws down an unsullied flesh-coloured precipitate from such solutions. It is not due to a trace of the higher salts, because treatment with reducing agents, for instance sulphurous acid, does not impair it.

It is not always easy to determine which is the normal oxide of a metal; reasoning, however, from analogy with iron, and from the reactions of the various oxides, we should be inclined to regard Mn_2O_3 as the normal oxide of manganese. This view is strengthened on consideration of the colour-properties of the metal, because the salts corresponding to MnO are colourless, or nearly so, as are the proto-salts of iron, copper, and chromium. On the other hand, the salts formed by dissolving Mn_2O_3 in cold hydrochloric or sulphuric acid are intensely coloured, resembling in this respect the salts of iron, cobalt,

* Statements regarding the colour of the proto-salts of manganese differ considerably.

nickel, copper, and chromium. Manganese in this form has a very high coefficient.

In describing the colour-properties of these elements I have always referred to dilute solutions. In dilute solutions the conditions are simplest, just as gases that obey Boyle and Mariotte's laws when remote from their condensing points fail to obey it when on the point of becoming liquids, so metallic salts in dilute solution and completely hydrated exhibit their characteristic colours, which sometimes become disturbed or undergo abrupt transitions when by concentration or increase of temperature the state of hydration of the salts becomes altered.

Solutions of chromium salts have a variety of colours; they may be green, blue, violet, or red, or of any intermediate tint. If to 10 c.c. of a solution containing 5 grams of chromium per litre, prepared by reducing potassium bichromate with sulphuric acid and alcohol, excess of caustic potash be added until the precipitate redissolves, a yellowish-green solution is obtained, and this reacidulated with sulphuric acid becomes bluish-green. If the 10 c.c. after treatment in this manner be added to 100 c.c. in a flask, a solution containing 0.5 gram of chromium per litre is obtained, and this solution when mixed with cobalt produces an optically neutral, but partially opaque, liquid. If 6 c.c. of cobalt (0.5 gram Co = 1 litre) be taken, about 25 c.c. of the chromium solution (0.5 gram Cr = 1 litre) will be required to produce optical neutrality, so that the colour-coefficient of chromium in this form is rather high.

The red salts of chromium may be prepared by the action of ammonia. This alkali, added in excess to a solution of chromium sulphate, precipitates a portion of the chromium as hydrate and retains the remainder in solution. The liquid filtered from the precipitate is reddish-purple, but becomes red on addition of sulphuric acid; a little sulphurous acid increases the purity of the tint. The sulphurous acid may afterwards be oxidised by nitric acid. The red salts of chromium so obtained strongly resemble dilute cobalt solutions, and like them are complementary to the green mixture of copper and iron (in equivalent colour-proportions) with which they form by admixture a grey liquid. Thus there seems to be in chromium salts a tendency to become identical in colour with the green mixture of 7 parts of iron and 20 parts of copper on the one side and with solutions of cobalt on the other. But it is possible to obtain chromium solutions of a different character. Moderate excess of ammonia added to a chromium sulphate solution dissolves, as we have seen, a portion of the precipitate forming the red solutions, but the chromium hydrate left undissolved is frequently of a blue colour, and gives when dissolved in sulphuric or nitric acid a blue solution. If instead of filtering the precipitate from

the ammoniacal liquid we reacidulate the whole with sulphuric or nitric acid, we obtain a violet solution approaching more nearly to pink, according as the solution is dilute and the amount of ammonia large, but possessing a full violet tint under some circumstances. These violet chromium solutions mixed with the green chromium solutions or with the green mixture of copper and iron in certain proportions, give blue chromium solutions. The red element in the violet solution is neutralised by the complementary green solution, a certain amount of opacity is conferred upon the liquid, and blue remains and is added to this. The blue solutions of chromium, as far as my experience enables me to judge, always have this characteristic. The amount of total absorption depends upon the quantities of the red and blue modifications that have neutralised, and the amount of blueness varies, being sometimes so small that the liquid has only a slate colour. The blue chromium salts appear to be identical in colour with the salts of copper, since a plate of copper viewed through them is perfectly white. It is easy to imitate the blue chromium salts by mixing copper solutions with the optically neutral liquid.

I have found it by no means easy to obtain the chromium salts in a state of perfect purity as regards colour; the red salts manifest on standing a tendency to become violet; the green salts are more easily obtained in a state approaching purity, but the solutions operated upon must be dilute. With manganese as with chromium, my experiments have hitherto been qualitative only; but they are sufficient to show that manganese forms modifications differing in their chromatic properties. These are obtained by dissolving the mixture of oxides prepared by the action of caustic alkali and alkaline hypochlorite on manganous salts. Under some circumstances, the manganese oxides catalyse the excess of hypochlorite; under other circumstances, the catalysis is arrested, and formation of permanganate of the alkaline base sets in. If the former condition of things is established and the precipitate is boiled for some time with the liquid, washed on a filter, and then dissolved in cold concentrated sulphuric acid, a pinkish-red solution, undistinguishable from a cobalt solution, is obtained. This solution is complementary to the green mixture of copper and iron, and gives by admixture with it a liquid, in most cases grey, but sometimes grey with a little tinge of yellow. These pink salts of manganese are permanent for some days in the cold, but the colour gradually fades, and is instantly destroyed by the introduction of caustic potash in quantity insufficient to neutralise the free sulphuric acid.

By dissolving the precipitated oxides of manganese in cold concentrated hydrochloric acid, brown solutions are produced, which, on dilution, become brownish-yellow. Manganese in this form is possibly analogous to the blue salts of chromium, inasmuch as they are opaque.

The brownish-yellow salts of manganese are exactly imitated by a mixture of iron and cobalt, with the optically neutral liquid. They are not, as far as I have seen, similar in colour to the mixture of iron and cobalt which is complementary to the salts of copper; they approach more nearly to iron. The following table exhibits the colour-properties of these elements, as studied up to the present; elements with solutions of similar colour are given in vertical lines:—

Yellow.	Orange.	Pinkish-red.	Violet.	Blue.	Green.
Fe Mn?	(7Fe + 6Co) Copper reflection Mn (nearly)	Co Cr Mn	(20Cu + 6Co) Cr mixture	Cu Cr	20Cu + 7Fe Cr Ni (nearly)

These combinations give grey partially opaque liquids:—

Cobalt, iron, and copper.
 Copper solutions and copper reflection.
 Chromium (blue) and copper reflection.
 Copper, iron, and chromium (red).
 Copper, iron, and manganese (red).
 Chromium (green) and chromium (red).
 Chromium (green) and cobalt.

These grey liquids, excepting the first, I have not specially examined; the first has been submitted to a few experiments. It is within wide limits of the same neutral tint in all thicknesses, and the amount of light absorbed increases with the thickness of the liquid traversed.

This mixture will probably be found useful in the analysis of light from various sources; a candle flame seen through a column of it appears greenish-yellow, and a red-hot platinum wire appears of a bright lemon-yellow colour when viewed in the same manner. The solution retains its greyness when evaporated considerably; a special description of its properties will, I hope, form the subject of a future communication to the Society.

The accompanying diagram (p. 386) shows the absorption spectra of cobalt, copper, and iron. The solutions were of equivalent chromatic strength, so that equal volumes of the three mixed together formed a grey liquid.* Equal thicknesses of each were placed separately in front of the slit of the spectroscope, and the resulting spectra are shown in the diagram.

* The best method of observing all the conditions of the absorption of metallic solutions is that of Gladstone; but in comparing the effects of various metals the solutions should contain the metals in the proportions of their colour-equivalents.

The study of the absorption spectra of the various modifications of manganese and chromium confirms the results already described. The absorption spectra of the green salts of chromium are shown in the diagram; it will be seen that the spectrum is complementary to the cobalt spectrum; the solution was not quite pure (chromatically): hence the presence of the faint band of red. The red salts of chromium and of manganese give spectra containing the red and violet rays, and a dark band occupying the place of the dark band in the cobalt spectrum. The blue salts of chromium have an absorption spectrum resembling that of the copper salts. It is difficult to obtain the modifications of chromium and the red salts of manganese quite pure. The red salts of chromium, when not quite pure, have an excess of violet, probably because of the presence of the blue modification of chromium; the green salts often transmit the penetrating red rays referred to by Gladstone (*Chem. Soc. J.*, 10, 79), and the optically neutral mixtures of the red and green sulphates of chromium, when the latter salts are not quite pure, reveal in the 20-centimeter tube the presence of these red rays, although without the assistance of the tube the liquid may seem perfectly devoid of colour. The red appearance of chromium salts in great thickness must not be confounded with the differentiation of the salts into the red and green varieties.

The red manganese salts, when not quite pure, seem to transmit a smaller proportion of violet rays than the cobalt salts. My observations indicate that the red salts of chromium and manganese tend to become identical in colour with cobalt as they progress towards purity.

We may divide the spectrum into three regions; (1) the red region, that covered by the absorption of copper; (2) the region covered by the absorption of cobalt, which we may call the green; and (3) the violet region, covered by the absorption of iron. It is possible that three modifications of chromium exist, each absorbing the rays contained in one of these three regions; the blue salts of chromium absorb the rays in the red region, and the red salts those in the green region; and there are possibly yellow salts capable of absorbing the rays of the violet region. The presence of such yellow salts in company with the blue and red salts would account for the suppression of white light effected by chromium salts. A green chromium solution, chromatically equivalent to a certain green mixture of iron and copper sulphates, is less transparent than the latter mixture is, and the same is true of the blue chromium salts.

In the same way it is possible there may be three modifications of manganese, the red salts, the yellow salts, the existence of which is indicated by the nature of the orange solutions of manganese, and unknown blue salts, which, existing only in combination, impart to manganese solutions the opacity they sometimes, if not always, possess.

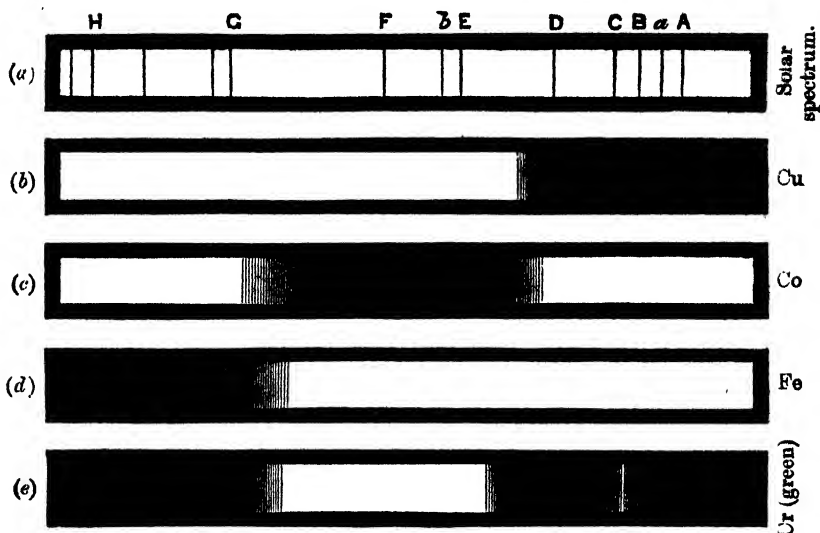


DIAGRAM SHOWING THE COMPARATIVE EFFECTS OF METALLIC SOLUTIONS OF EQUIVALENT COLOUR STRENGTHS.

The following conclusions appear to be fairly deducible from the experiments described in this paper:—

There are intimate relations between the metals Cr, Mn, Fe, Ni, Co, and Cu.

Absorption and transmission of light by solutions of the salts of these metals take place in three definite regions of the spectrum; these regions are shown in the diagrams (b), (c), and (d).

Each of the metals Fe, Co, and Cu forms salts, corresponding to one oxide, which are *usually* of one distinctive colour, and absorb light in one of the three regions of the spectrum.

Nickel salts are *usually* green, and have two absorption bands.

Each of the two elements (with least atomic weight), viz., Cr and Mn, forms more than one kind of salt, each kind identical in colour-properties with the salts of one of the three elements Fe, Co, and Cu, or with a mixture of two of these elements of definite composition, and complementary in colour to the third.

In the case of Fe, Co, Ni, and Cu, the mean wave-length of the light absorbed is a function of the atomic weight.

In the case of the sulphates of the same four metals, the colour-coefficient or specific chromatic power of each element is independent of the atomic weight, and is greater than the colour-coefficient of any other of the four elements having a less affinity for oxygen, and less than the coefficient of any element with a greater affinity for oxygen.

The colour-coefficient varies, in some cases at least, with temperature, with the nature of the acid radical, and with the state of oxidation.

PROCEEDINGS
AT THE
MEETINGS OF THE CHEMICAL SOCIETY,
SESSION 1879-80.

November 6th, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

“On the Transformation-products of Starch:” by C. O’Sullivan.

“On the Formulæ of Carbohydrates:” by H. E. Armstrong.

“On a New Method of Determining Sulphur in Coal:” by Teikichi Nakamura, of Tokiô.

“On the Bromine-derivatives of β -Naphthol:” by A. J. Smith.

“On the Dissociation of Ammonia-alum:” by J. S. Thomson.

“On α -Methyloxysuccinic Acid, the Product of the Action of Anhydrous Hydrocyanic Acid upon Aceto-Acetic Ether:” by G. H. Morris.

“On the Action of Phosgene on Ammonia:” by H. J. H. Fenton.

“On the Rehydration of Dehydrated Metallic Oxides:” by C. F. Cross.

“On Alizarin Blue:” by G. Auerbach.

November 20th, 1879.

Dr. J. H. Gilbert, Vice-President, in the Chair.

The following papers were read:—

“A Chemical Study of Vegetable Albinism” (Part II). “Respiration and Transpiration of Albino Foliage:” by A. H. Church.

“Contributions to the History of Putrefaction” (Part I): by C. T. Kingzett.

“Notes on Manganese Dioxide:” by C. R. A. Wright and A. E. Menke.

"On the Reaction between Sodium Thiosulphate and Iodine."
"Estimation of Manganese Oxides and Potassium Bichromate:" by
Spencer U. Pickering.

December 4th, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"On the Comparative Value of Different Methods of Fractional Distillation:" by F. D. Brown.

"On the Influence exerted upon the course of Certain Chemical Changes by Variations in the Amount of Water of Dilution:" by M. M. P. Muir.

"On the Influence of Temperature upon the Decomposition of Barium Chloride by Potassium Oxalate in Aqueous Solution:" by M. M. P. Muir.

"On α - and β -Phenanthrene-carboxylic Acids:" by F. R. Japp.

"On Some Derivatives of Phenylacetic Acid:" by P. Phillips Bedson.

December 18th, 1879.

Dr. Warren De La Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

G. S. Allbright, Mariemont; J. R. Ashwell, Nottingham; T. Blackburn, Darlington; E. Buckney, Brunswick Square, S.E.; J. Bemrose, Montreal; W. J. F. Churchouse, Somerset; M. Cochrane, Ceylon; E. J. Day, Dorchester; W. R. Dunstan, St. Peter's Park, W.; E. Francis, Chesterfield; F. Hatton, Titchfield Terrace, N.W.; J. Howard, Southgate Grove, N.; J. J. Hummell, Leeds; R. E. Holloway, St. John's, Newfoundland; W. R. Eaton Hodgkinson, Sheffield; T. S. Humpidge, Aberystwyth; E. Hughes, Montgomeryshire; R. Jones, Salford; J. Knowles, Tottington; A. Leibius, Sydney; H. F. Morley, Haverstock Hill, N.W.; E. F. Mondy, Salop; H. Newton, Singapore; J. Paretta, Monmouthshire; J. W. Smith, Fulham; J. Steiner, Leeds; J. Snodgrass, Glasgow; A. Scott, Trinity College, Cambridge; G. Shallard, St. Paul's School, E.C.; J. M. Wilson, Alexandra Park.

The following papers were read:—

"On the Specific Volume of Water of Crystallisation:" by T. E. Thorpe and J. I. Watts.

"Note on the Formation of Ozone during the slow Combustion of Phosphorus:" by Herbert McLeod.

"On the Analysis of Organic Bodies containing Nitrogen:" by W. H. Perkin.

January 15th, 1880.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"On the Effects of the Growth of Plants on the Amount of Matter removed from the Soil by Rain:" by E. W. Prevest.

"On Dibromanthraquinones:" by W. H. Perkin.

"On the Melting and Boiling Points of Certain Inorganic Substances:" by T. Carnelley and W. C. Williams.

February 5th, 1880.

Dr. Warren De La Rue, President, in the Chair.

The following papers were read:—

"Note on the assumed Formation of Ozone by Atmospheric Oxidation of Phosphorus:" by C. T. Kingzett.

"Contributions from the Laboratory of the University of Tôkiô, Japan." II. "On Perthiocyanate of Silver:" by R. W. Atkinson.

"On Methylated Dioxethylenamines:" by H. F. Morley.

"Note on Igasurine:" by W. A. Shenstone.

"On Some Reactions of Tertiary Butyl Iodide:" by L. Dobbin.

February 19th, 1880.

Dr. Warren De La Rue, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

J. C. Evans, Shaftesbury Park; W. H. Glazier, Finchley Road, N.W.; J. Hogarth, Ardrossan; K. W. Hedges, Streatham Hill; R. Howell, Surbiton; A. Lloyd, Haverstock Hill, N.W.; W. Macnab, Clifton Road, N.W.; A. K. Miller, Hampstead; J. McCarthy, Trinidad; G. H. Morris, Bristol; P. Matthews, Stourbridge; W. O. Prosser, Swansea; H. F. Pasley, Lancashire; W. B. Roberts, Shepherd's Bush, W.; G. Salet, Paris; A. G. Salamon, Clapham Park, S.W.; T. Terrell, Notting Hill; E. Wilcock, Camberwell, S.W.; W. H. Wood, Halifax.

The following papers were read :—

“ On the Production of Ozone during the Combustion of Coal Gas : ”
by R. H. Ridout.

“ Some New and Improved Laboratory Appliances : ” by R. H. Ridout.

“ A reply to the criticism of Mr. Kingzett on the Formation of Ozone during the Slow Combustion of Phosphorus, ” was made by H. McLeod.

“ Remarks on the so-called Unsaturated Organic Compounds : ”
by H. E. Armstrong.

March 4th, 1880.

Dr. Warren De La Rue, President, in the Chair.

Prof. T. E. Thorpe delivered a lecture “ On the Relation between the Molecular Weights of Substances and their Specific Gravities when in the Liquid State. ”

March 18th, 1880.

Dr. Warren De La Rue, President, in the Chair.

A paper was read “ On River Water : ” by Dr. Tidy.

March 30th. Anniversary Meeting. (See p. 246).

April 1st, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read :—

“ On Betoreinol and some of its Derivatives : ” by J. Stenhouse and C. E. Groves.

“ Note on Chemical Equilibrium : ” by M. M. P. Muir.

“ Preliminary Note on the Action of the New Diastase, Eurotin, in Starch : ” by R. W. Atkinson (Tôkiô).

“ Note on the Products of the Combustion of Coal-gas : ” by L. T. Wright.

“ On the Polysulphides of Sodium : ” by H. Chapman Jones.

“ On the Reflection from Copper, and on the Colorimetric Estimation of Copper by Means of the Cuprimeter : ” by T. Bayley.

"On Pyrene:" by Watson Smith and G. W. Davies.

"On the Analysis of the Ash of the Wood of Two Species of Eucalyptus:" by Watson Smith.

"On the Action of Organo-zinc Compounds on Quinones:" by F. R. Japp.

April 15th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society:—

M. Bechler, Hammersmith; A. E. Black, Glasgow; E. C. Copas, Isle of Man; W. J. Dibdin, Shepherds' Bush, W.; A. C. Fryer, Cheshire; C. C. Graham, Tulse Hill, S.W.; C. H. Ginringham, St. Augustine's Road, N.W.; R. Grimwood, Oxford Street, W.; W. F. Haydon, Worcestershire; H. Liepmann, Glasgow; F. B. Last, Liverpool; W. Robinson, Bridgewater; W. Regester, Isleworth; J. W. Stanley, Glamorgan; H. H. Slater, Maidstone; A. J. Smith, Woolwich; H. C. Stephens, Finchley; C. P. Scheibner, Charles Street, Grosvenor Square; J. R. Skelton, Essex.

The following papers were read:—

"On the Lecture Illustrations of Chemical Curves:" by E. J. Mills.

"On the Analysis of Organic Bodies containing Nitrogen" (continued): by W. H. Perkin.

"On the Volatilisation of Solids *in vacuo*:" by W. Douglas Herman.

"On the Determination of Nitric Acid as Nitric Oxide by means of its Reaction with Ferrous Chloride:" by R. Warrington.

"On the Influence of the Amido-group upon the Orientation of Bromine or NO_2 in the Benzene-nucleus, as illustrated by the preparation of the six possible Dibromotoluenes, the six possible Tribromotoluenes, the three possible Tetrabromotoluenes, and various other Bromo- and Bromonitro-derivatives of Toluene:" by R. Neville and A. Winther.

May 6th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Action of Sodium on Phenylacetic Acid:" by W. H. Perkin, Jun., and W. R. Hodgkinson.

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"Preliminary Notice on the Action of Sodium on some Ethereal Salts of Phenylacetic Acid:" by W. R. Hodgkinson.

"On the Determination of Nitrogen in Organic Bodies:" by C. E. Groves.

"On Essential Oil of Sage:" by M. M. P. Muir.

"On the Presence of Nitrogen in Iron and Steel:" by A. H. Allen.

"On the Mode of Application of Pettenkofer's Process for the Determination of Carbonic Acid in Expired Air:" by W. Marcet.

"Note on an Improved Form of Oven for Heating Sealed Tubes and Avoiding Risks of Explosions:" by Watson Smith.

"Note on a Convenient Form of Lead-bath for Victor Meyer's Apparatus for determining the Vapour-densities of High-boiling Substances, together with a Few Slight Modifications:" by Watson Smith.

May 20th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On the Action of Air upon Peaty Water:" by Lucy Halcrow and E. Frankland.

"On the Spontaneous Oxidation of Organic Matter in Water:" by E. Frankland.

June 3rd, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following papers were read:—

"On some Products of the Oxidation of Paratoluidine:" by W. H. Perkin.

"On the Detection of Foreign Colouring Matters in Wine:" by A. Dupré.

"On the Action of Organo-zinc Compounds on Nitriles and their Analogues. I. Action of Zinc ethyl on Azobenzene:" by E. Frankland and D. A. Louis. II. "On the Action of Zinc ethyl on Benzonitrile:" by E. Frankland and J. Castell Evans.

"On the Relation between the Molecular Structure of Carbon Compounds and their Absorption Spectra:" by W. N. Hartley.

"On a Simple Method of Determining Vapour-densities in the Barometer Vacuum:" by C. A. Bell and F. L. Teed.

June 17th, 1880.

Prof. H. E. Roscoe, President, in the Chair.

The following gentlemen were duly elected Fellows of the Society :—

P. S. Brown, Leven; H. Brown, University College, W.C.; K. dal Rey Rai Bahadour, Calcutta; G. H. Hughes, Barbadoes; H. A. Lawrance, Islington; F. E. Matthews, Hildrop Road, N.; E. Moritz, Highbury Quadrant, N.; R. S. Marsden, Sheffield; E. A. Reilly, Uxbridge; Tarapwsanna Roy, Calcutta; C. Rawsen, Cirencester; B. Symons, Servia; J. Taylor, Manchester; H. K. Tompkins, Dulwich; R. G. Watts, Bulstrode Street, W.; A. Wingham, Borough Road, S.E.

The following papers were read :—

“On Pentathionic Acid :” by T. Takamatsu and Watson Smith.

“Preliminary Note on some Orcinol-derivatives :” by J. Stenhouse and C. E. Groves.

“On the Determination of Carbon in Soils :” by R. Warington and W. A. Peake.

“Note on Camphydrene :” by H. E. Armstrong.

“On the Action of Nitric Acid upon Diparatolylguanidine :” by A. G. Perkin.

“On some Higher Oxides of Manganese and their Hydrates :” by V. H. Veley.

“On a New Method of Preparing Dinitroethylic Acid :” by E. Frankland and C. E. Graham.

“On the Action of Organo-zinc Compounds upon Nitriles and their Analogues :” by E. Frankland and H. H. Tompkins.

“On the Action of Benzoyl Chloride on Morphine :” by C. R. A. Wright and E. H. Rennie.

“An Examination of Terpenes for Cymene by means of the Ultra-violet Spectrum :” by W. N. Hartley.

“Note on the Purple of the Ancients :” by E. Schunck.

Donations to the Library, 1879–80 :—

“Wilson’s Inorganic Chemistry, with New Notation :”

from the Publishers.

“The Rise and Development of Organic Chemistry :” by C. Schorlemmer : from the Author.

“Guia para el Analisis immediate de los Vegetales :” por Pedro N. Arata : from the Author.

"Water-Analysis for Sanitary Purposes:" by E. Frankland, Ph.D., F.R.S.: from the Author.

"Lightning Conductors:" by Richard Anderson: from the Author.

"Attfield's Manual of Chemistry." 8th edition:

from the Publisher.

"A Handy Book of Forensic Medicine and Toxicology:" by Dr. W. D. Woodman and Dr. C. M. Tidy: from the Authors.

"The River Tyne: its History and Resources:" by James Guthrie: from the Tyne Improvement Commissioners.

"Historical Sketch of the Progress of Pharmacy in Great Britain:" by Jacob Bell and Theophilus Redwood:

from the Pharmaceutical Society.

"Introduction to the Study of Organic Chemistry:" by Henry E. Armstrong. 2nd edition: from the Author.

"Chemical Notes:" by Sydney Lupton: from the Author.

"Table of Logarithms on Card:" by Sydney Lupton:

from the Author.

"Introduction to the Study of Chemical Philosophy:" by Dr. W. A. Tilden: from the Author.

"The Chemist's Manual:" by H. A. Mott: from the Author.

"Recherches sur l'Electricité:" par Gaston Planché:

from the Author.

"Diè Naturgesetze, 3te Abtheilung:" von Dr. H. Schaffler:

from the Author.

"Practical Chemistry and Quantitative Analysis:" by Dr. F. Clowes: from the Author.

"A Hand-book of Chemical Manipulation (Supplement):" by C. Greville Williams: from the Author.

"A Geological Survey of Indiana:" by E. T. Cox, State Geologist: from the Author.

"Nature's Hygiene:" by C. T. Kingzett: from the Author.

"A Pocket Mining Atlas:"

from the Scientific Publishing Company of New York.

"Descriptive Atlas of the Eucalypts of Australia:" by Baron F. von Müller.

"Canton Lectures: Chemistry of Bread-making:" by Dr. C. Graham: from the Author.

Pamphlets:—

"On Photographing the Spectra of the Stars and Planets:" by W. H. Draper: from the Author.

"On the Coincidence of Bright Lines in the Oxygen-spectrum with Bright Lines in the Solar Spectrum:" by W. H. Draper:

from the Author.

"The 'Thunderer' Gun Explosion:" by F. J. Bramwell:

from the Author.

"Sur l'Isotributylène:" par A. Boutlerou: from the Author.

"Recherches sur la Constitution des Hydrates ferriques."

"Reduction du Chlorure d'Argent."

"Sur la Non-existence de l'Hydrogène naissant."

"Nuove Prove in conferma alla teoria termica sullo stato nascente dell' Idrogeno."

"Sull Equilibrio termico delle Azione chimiche."

"Ricerche sulle Formule di Costituzione dei Composti ferrici. Parte I. Idrati ferrici:"

di Donato Tommasi: from the Author.

Periodicals:—

"Philosophical Transactions for 1879:" from the Royal Society.

"Transactions of the Royal Society of Edinburgh." Vol. xxix, Part I: from the Society.

Proceedings of the same. Session 1878-1879: from the Society.

"Report of the British Association for the Advancement of Science for 1879:" from the Association.

"Proceedings of the Physical Society of London." Vol. iii, Part 3. November, 1879, to February, 1880: from the Society.

"Journal of the Royal Microscopical Society, 1880:"

from the Society.

"Journal of the Iron and Steel Institute, 1879:"

from the Institute.

"Sessional Proceedings of the Social Science Association, June, 1880:" from the Association.

"The Journal of Medicine, according to Dr. Barggreave's Dosimetric Method:" edited by Dr. T. L. Phipson.

"Proceedings of the Philosophical Society of Glasgow, 1878-79:" from the Society.

"The Chemical News, 1879-80:" from the Editor.

"Journal of the Society of Arts, 1879-80:" from the Society.

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ERRATA.

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42	1	<i>for loss read no loss.</i>
500	1	„ correction of the vol. of air in cylinder for 2° F. = 15 c.c.
		<i>read correction</i> „ „ „ = 8 c.c.

This will make the result on p. 500, line 7—

$x = 0.436$ gram CO_2 *instead of* 0.435 gram CO_2 .

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